New Materials from Waste and Renewable Oils

By
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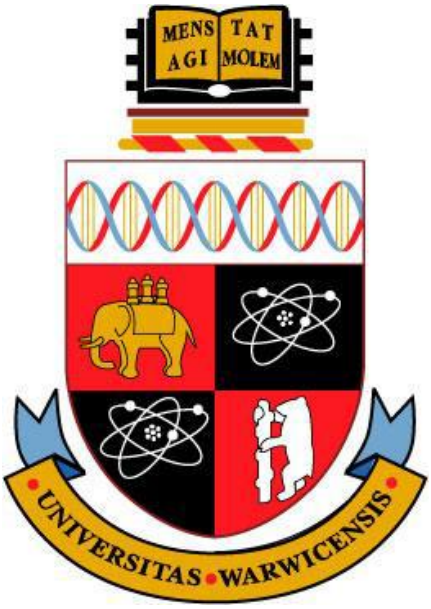

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This thesis is dedicated to those members of my family who are no longer around to see me complete my PhD.

Declaration

The work presented in this thesis is the original work of the author. Reference to previous related results and ideas has been fully acknowledged. All work was performed in the Department of Chemistry at the University of Warwick between October 2010 and June 2014 and has not been submitted for a degree at any other institution.

Andrew Sellars

Abstract

The work presented in this thesis represents the chemical modification of waste and renewable vegetable oils to yield monomers for polyurethane, azide-alkyne click and nitrile-oxide click polymerisations. Chapter 1 provides a brief introduction to use of waste materials for new products, following on to a more detailed overview of triglyceride chemistry, finishing with an introduction to 'Click' chemistry.

Chapter 2 discusses the optimisation studies of acid catalysed ring-opening of epoxidised cocoa butter followed by polyurethane synthesis. Percentage of ring-opening was found to be influenced by the amount of phase-transfer catalyst, concentration of reaction and equivalents of acid. Mechanical properties (Young's Modulus (YM), Tensile strength (TS) and Elongation at break (EoB)) were determined and thermal analysis (TGA, DSC) measured on cocoa butter based polyurethanes both with and without food-safe dyes as an alternative more environmentally friendly renewable oil source for polyurethane synthesis.

Chapter 3 focuses on the use of azide-alkyne click chemistry to produce renewable polymers from dimeric fatty amides (capable of H bonding) with increasing linker length and azide functionality. Samples were synthesised from purified oleic acid and linoleic acid and cheaper, more commercially available rapeseed oil and soybean oil. Thermal properties (TGA, DSC) of copper mediated and thermally produced polymers were analysed and mechanical properties (YM, TS and EoB) of thermally produced polymers were also investigated showing increasing linker length increased elongation and decreased tensile strength and also showed the importance of H bonding between polymer chains drawn.

Chapter 4 expands on azide-alkyne click polymerisation by synthesis of a range of monomers containing both azide and alkyne units therefore capable of homopolymerisation. Increasing chain length, azide functionality and hydrogen bonding possibilities were again tested using the same four starting materials as Chapter 3 as well as increasing cross-linking possibilities and results were found to compare with those established in Chapter 3.

Chapter 5 concentrates on using nitrile oxide-alkyne click polymerisations as an alternative and safe method of producing renewable polymers derived from vegetable oils. Two approaches were used for polymerisations, base mediated and thermal mediated polymerisations with polymers produced subjected to thermal analysis (TGA, DSC).

Chapter 6 describes the experimental and chemical analysis of the key reactions and processes described in the thesis.

Abbreviations

br	Broad
$CDCl_3$	Deuterated Chloroform
$CHCl_3$	Chloroform
DCM	Dichloromethane
DSC	Differential Scanning Calorimetry
d	Doublet
dd	Doublet of doublets
ddd	Doublet of doublet of doublets
DMF	Dimethylformamide
dt	Doublet of triplets
EoB	Elongation of break
ES	Electrospray Ionisation
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
EtOH	Ethanol
FM	Flexural Modulus
GPC	Gel Permeation Chromatography
h	Hours
hex	Hexane
H_2O_2	Hydrogen Peroxide
Hz	Hertz
IR	Infra-Red
K_2CO_3	Potassium Carbonate
m	Multiplet
min	Minutes

MDI	4,4’-methylene bis(phenyl isocyanate)
Mn	Number average Molecular weight
MPa	Mega Pascal
M_w	Weight average Molecular weight
N_2	Nitrogen
NaH	Sodium Hydride
NaN_3	Sodium Azide
NaOH	Sodium Hydroxide
NaOMe	Sodium Methoxide
NH_4Cl	Ammonium Chloride
NMM	*N*-methylmorpholine
NMR	Nuclear Magnetic Resonance
OH	Hydroxyl Group
OHV	Hydroxyl Value
p	Pentet
PD	Polydispersity Index
PET	Polyethylene Terephthalate
pet ether	Petroleum ether 40-60 °C
ppm	Parts per million
PU	Polyurethane
q	Quartet
s	Singlet
SeO_2	Selenium Dioxide
t	Triplet
t-BuOOH	tert-Butyl hydroperoxide
TEA	Triethylamine

T_g	Glass Transition Temperature
TGA	Thermo gravimetric analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TS	Tensile strength
YM	Young's Modulus

1.0 Introduction

As the demand for crude oil increases, and oil reserves deplete, the need for renewable materials grows ever more important. Renewable materials primarily come from biomass. Biomass is biological material from living or recently living organisms, mainly plants, and is comprised of wood, plants, landfill gases, household waste and alcohol fuels. Bioplastics are a form of plastic derived from biomass sources, predominantly from vegetable oils and fats, wood (lignin and cellulose) and starch (corn, potato and rice) and have received a lot of attention in recent years as alternatives to petrochemical based polymers. Alternatively waste polymer recycling has attracted attention as a way of reducing the use of petrochemicals to produce polymers. There are two routes of recycling plastics: mechanical recycling,[1] where plastics are ground down and reprocessed for either same or similar use, and chemical recycling[2] where the plastics are turned back into the original components which can be reused to make new materials.

There is a long history of using waste renewable products from one industry to make useful materials for another.[3-8] A brief review is given of examples from different areas but this introduction will primarily focus on the use of oils and fatty acids as feedstocks for polymer synthesis.

1.1 Carbohydrates

Starch: In 2002 Doi *et al.* used starch to synthesise catalysts (Fig. 1.1) for liquid phase organic reactions (e.g. the Knoevangel reaction, Fig. 1.2).[3] The results

compared well with traditional catalysts (eg pyridine) and showed that corn starch could be used as a porous heterogeneous catalyst.

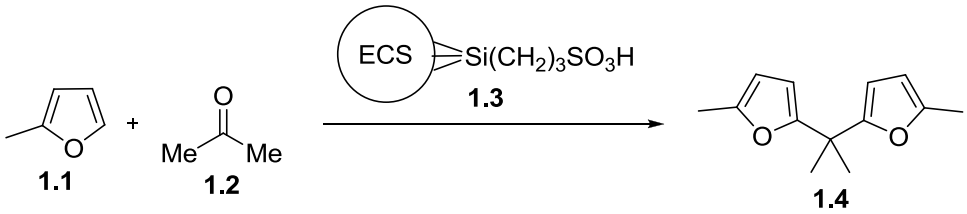


Figure 1.1

Figure 1.1: Reaction of acidic ECS with 2-methylfuran and acetone.[4]

In 2004 Milkowski *et al.* used expanded corn starch (ECS) in a graft-polymerisation reaction of a range of synthetic monomers.[5] The ECS was modified in three ways, one using a glycidyl methacrylate, another using epichlorohydrin and the third using chlorosulfonic acid. The three types were tested with styrene, α-methyl styrene and methyl acrylate. The copolymers produced in this method showed improved thermal properties when compared to the traditional grafts and showed that not all polymers have to be made by 100 % synthetic monomers.

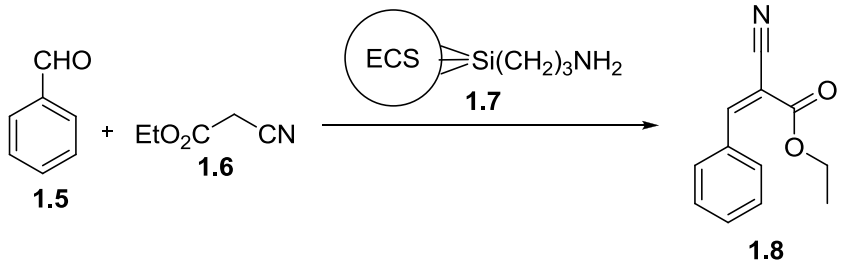


Figure 1.2: Knoevenagel reaction using ECS base.[3]

In 2009 Shuttleworth *et al.* attempted to use starch based adhesives in the textile industries as binders to join aluminium together.[6] It was shown that starch can be

used as an adhesive when it has been heated to 250 °C as it contains a special transition point at that temperature and just below this the starch decomposes, without CO or CO_2 production, to form polymers with good adhesion and cohesion properties.

In 2010 Ismanto *et al.* prepared capacitor electrodes from cassava peel waste.[7] Cassava is a root vegetable from tropical and subtropical regions. The dried waste peel from these roots can be activated for use as electrodes. Activation with potassium hydroxide and surface modification using nitric acid, sulfuric acid and hydrogen peroxide followed by physical activation using heat lead to the formation of activated carbon products. Electrodes were then produced from the products and were found to form high performance and low cost activated carbon electrode materials for electric double layer capacitors.

Also in 2010 Ibrahim *et al.* used banana plant waste as reinforcements in polymer composites.[8] The banana plant waste was treated with alkaline pulping or steam explosion to produce banana fibres and microfibrils. Some of the fibres/microfibrils were further modified with maleic anhydride (Fig. 1.3) to form maleated lignocellulosic fibres which were used to reinforce a polyethylene matrix.

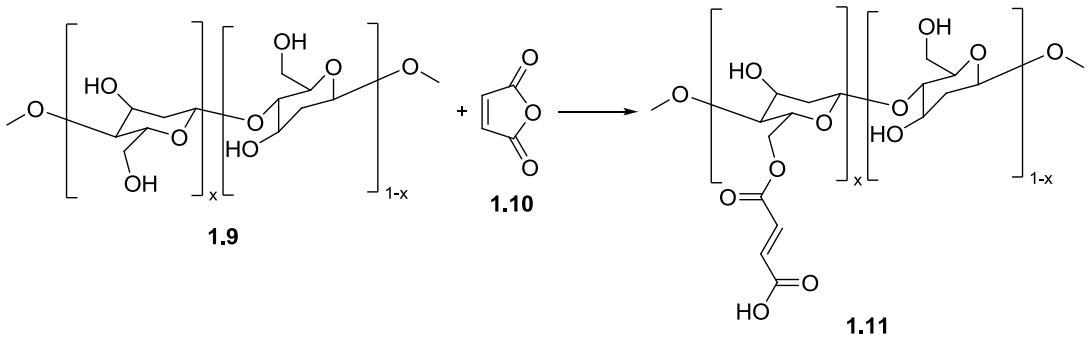


Figure 1.3: reaction between cellulose and maleic anhydride.[8]

It was found that the addition of 20% maleated fibres resulted in better adhesion to the polymer and therefore better tensile strength. The higher the crystalinity and lignin content of the steam exploded fibres also improved the tensile strength of the composites.

1.2 Waste Plastic Recycling

In 2009 Czub developed a method of degrading poly(ethylene terephthalate) (PET) waste to form new epoxy resins.[9] The waste PET was degraded by glycolysis to produce a range of products: glycols, monomer, dimer, trimer, tetramer and other oligomers. These waste materials were used in a reaction with epichlorohydrin to synthesise epoxy resins (Fig. 1.4 and 1.5).

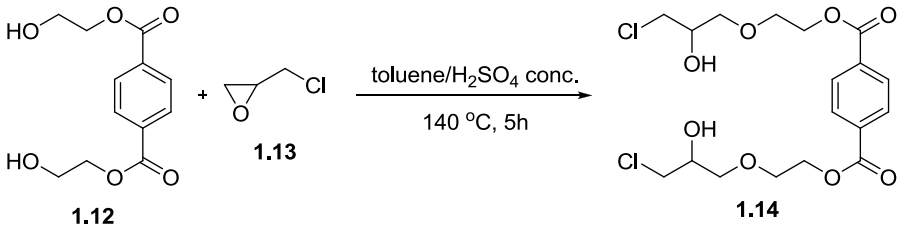
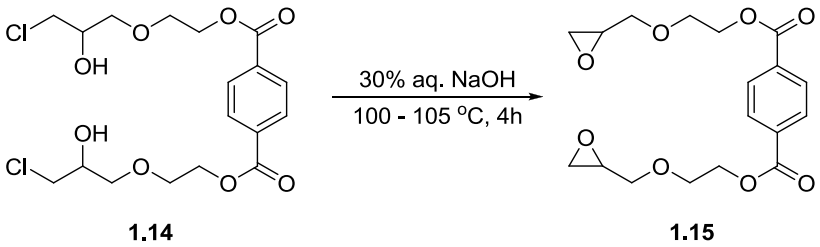


Figure 1.4: Reaction of PET glycolysis products with epichlorohydrin.[9]

The products were incorporated into Araldite® and Epidian® 5 epoxy resins low-molecular-weight epoxy resins and were shown to improve the tensile and flexural strengths as well as hardness and thermal stabilities. Czub concluded that it was possible to recycle PET to form new epoxy resins and longer chain glycolysis products had a greater effect on the properties of the epoxy resins than the shorter chained ones.



1.14 1.15

Figure 1.5: Dehydrohalogenation of modified PET glycolysis product.[9]

Later in 2009 Ashori investigated some thermoplastic biofibre hybrid composites from waste newspaper fibre (NF) and poplar wood flour (WF).[10] The composites consisted of a weight ratio of 30:70 lignocellulosic materials (newspaper fibre and poplar wood flour) to polymer. The polymer was made up of polypropylene (polymer matrix) and maleic anhydride grafted polypropylene (coupling agent). A series of composites were prepared with the NF:WF ratios of: 100:0, 75:25, 50:50, 25:75, 0:100. The coupling agent was added with respect to the total weight of the composite and deducted from the polypropylene content. Composites prepared with the coupling agent included showed better physical properties than those without. The composites produced showed that lignocellulosic materials could successfully be used as reinforcing elements in thermoplastic polypropylene matrix with better physical properties when compared to pure polypropylene matrix.

In 2011 Sadeghi *et al.* incorporated aminolysis products of PET waste into novel biodegradable polyurethanes.[11] The product from this aminolysis was Bis(2-hydroxyethylene) terephthalamide (BHETA) which the group found little reported usage in polyurethane synthesis. BHETA was used to produce polyols containing caprolactone with different molecular weights through the ring opening polymerisation of the caprolactone (Fig. 1.6).

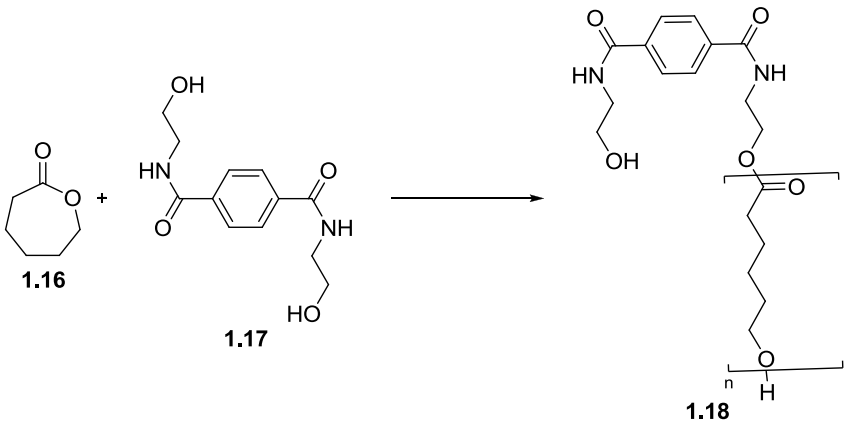


Figure 1.6: Polyol synthesis from caprolactone using BHETA.

The polyols were polymerised with hexamethylene diisocyanate (HDI) without a chain extender. Analysis showed that the longer the polyols and the higher the soft segment (caprolactone) the more crystalline the polyurethanes and the higher the melting point. Biodegradability tests also showed high rated biodegradation for all polyurethanes synthesised.

1.3 Wood and Agricultural Waste

A wide range of chemicals, such as bio-oils and syngas, have been prepared from the pyrolysis of wood and agricultural waste.[12] Bio-oils can be upgraded to transportation fuels, such as bioethanol and biodiesel.[13] Syngas can be converted to methanol, hydrocarbons, ammonia and used in power stations to provide electricity.[13-14]

1.4 Vegetable Oils

Vegetable oils are part of a family known as lipids. Lipids are comprised of many compounds such as fats, sterols, complex glycolipids and triglycerides. Triglycerides **1.19** (Fig. 1.7) are comprised of a glycerol component and three fatty acid chains with varying fatty acid compositions depending on the organism they are found in. In crops the fatty acid composition can change depending upon the variety, season and growing conditions.[15] The fatty acid composition (Table 1.1) can be determined by fatty acid methyl ester analysis (FAME) and fatty acids chains are identified with a number (C18:1 for oleic acid) where the first number corresponds to the number of carbons and the second number identifies the amount of unsaturation within the chain. These fatty acids can contain various reactive sites, such as alkenes, allylic and α carbons, carbonyl components, alcohols (if ricinoleic acid **1.25** is present) and epoxides (if vernolic acid **1.26** is present) (Fig. 1.8) making triglycerides versatile compounds from which to synthesise renewable materials. In 2011 Palm, soybean, canola and sunflower oil accounted for 72% of total global consumption of fats and oils.[16]

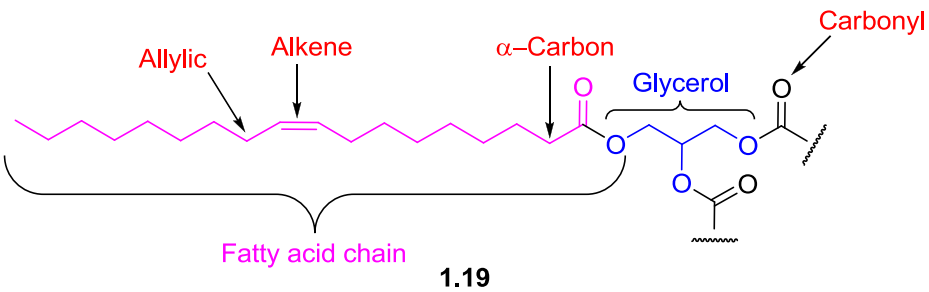


Figure 1.7: Triglyceride showing areas of functionality suitable for chemical modification.

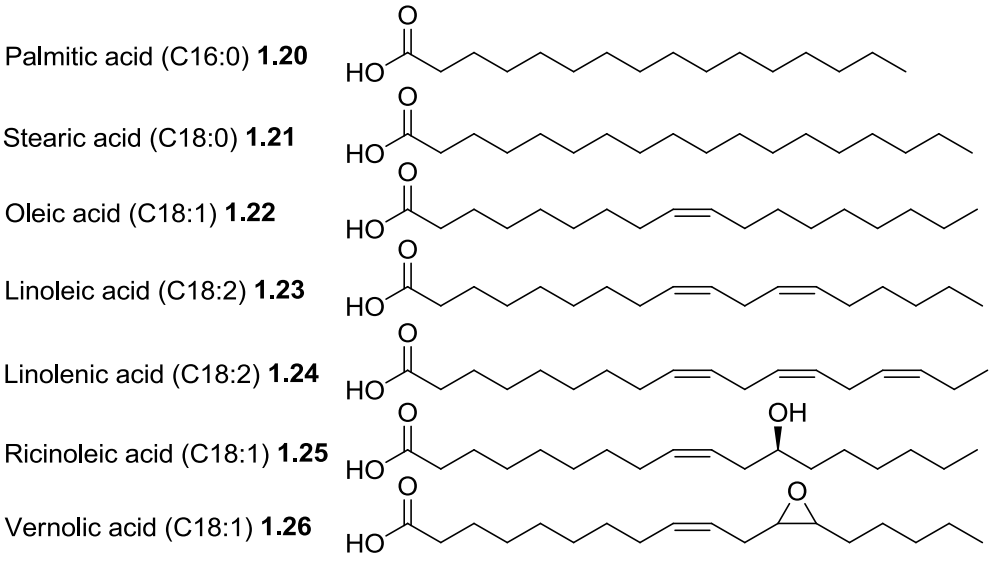


Figure 1.8: Common fatty acids present in vegetable oils.

Triglyceride	Fatty acid composition (%)				
	C16:0	C18:0	C18:1	C18:2	C18:3
Cocoa butter	26	34	35	-	-
Corn	13	3	31	52	1
Cottonseed	23	2	17	56	-
Linseed	6	3	17	14	60
Olive	10	2	78	7	2
Palm	44	4	39	11	-
Rapeseed	4	2	62	22	10
Safflower	7	3	14	75	-
Soybean	11	4	23	53	-
Sunflower	6	5	65	26	-

Table 1.1: Typical fatty acid compositions of a range of triglycerides.[17]

Carbonyl and alkene chemistry of triglycerides is particularly relevant to this project, therefore a brief summary of the chemistry of triglycerides is presented. This is not designed to be exhaustive but should give the reader an overview of the subject.

1.4.1 Reaction of the allylic carbon

The allylic carbon in the fatty acid chain is a potential site for oxidation, plays a key role in the autoxidation of fatty acids (see section 1.4.1.2) and can undergo allylic hydroxylation[18] and halogenation.[19] Hydroxylation of oleic acid **1.22** was achieved using SeO_2 and *t*-BuOOH in 24 hours at room temperature. The reaction gave a mixture of mono- (**1.27** and **1.28**) and di- hydroxylated (**1.29**) oleic acid as a mixture of diastereomers (Fig. 1.9).[20]

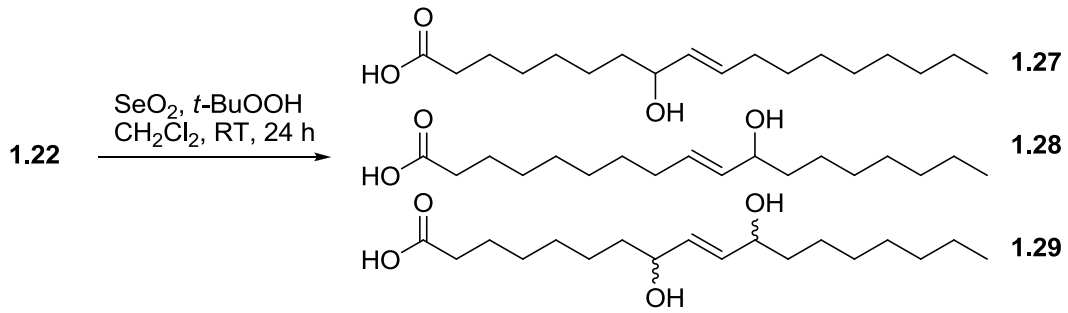


Figure 1.9: Allylic oxidation of oleic acid 1.22.[20]

1.4.2 Reactions at the carbonyl

1.4.2.1 Transesterification

Reactions at the carbonyl position of the fatty acid are one of the most common approaches in oleochemistry. Glycerolysis involves reaction of triglycerides with varying ratios of glycerol to produce mono- and di-glycerides (Fig. 1.10).[21]

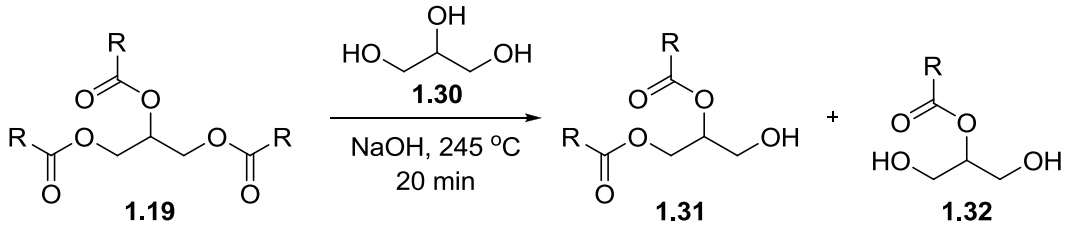


Figure 1.10: Glycerolysis of triglycerides.

Pyrolysis of triglycerides has been investigated for over 100 years especially in areas with limited or no petroleum reserves therefore is not relatively new[22] however, biorenewable fuels, such as biodiesel, from renewable oils have attracted a large amount of attention in recent years as a substitute to petroleum distillates and petroleum based petrochemicals, especially with the depletion of natural oil reserves.[23-25] Vegetable oil and animal fat are most commonly used in biodiesel synthesis. In triglyceride form the oils have low volatility and are far more viscous than conventional diesel, therefore have to be modified. Transesterification of renewable oils to fatty acid methyl or ethyl esters[26-27] (Fig. 1.11) increases the volatility of the oils and decreases the viscosity when compared to the vegetable oil, thus making it more closely resemble conventional diesel. The use of branched alcohols, such is isopropanol and 2-butanol, has also been employed to lower crystallisation temperatures.[28] Significant research has been reported into optimising the transesterification process by tailoring the catalyst and temperature.[29] Alkali catalysts are most common in this process due to faster reaction times and higher yield however, acidic and enzymatic[30-31] catalysed reactions can also be used as well as using microwave irradiation[32] in batch and flow processes to improve reaction times.

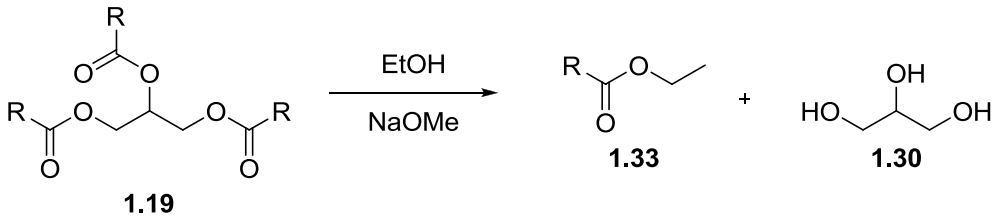


Figure 1.11: Synthesis of biodiesel.

1.4.2.2 Aminolysis

Aminolysis is a reaction between esters and amines to produce amides and can be achieved using metallic catalysts, such as sodium methoxide, biocatalysts or microwave irradiation.[33-37] In 1966, Gast *et al*. reacted linseed oil with diethanolamine using sodium methoxide catalyst at 110-115 °C (Fig. 1.12).[38]

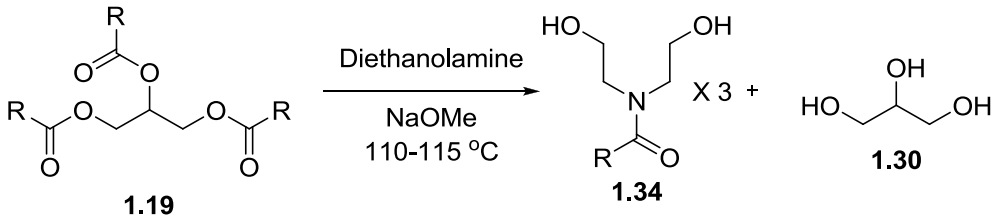


Figure 1.12: Aminolysis of triglyceride with diethanolamine.

The diethanolamides synthesised were used to produce viscous oil polyesters for use in protective coatings. Thirty years later, de Zoete *et al*. reported the aminolysis of olive oil using ammonia saturated *t*-butanol and *Candida antarctica* lipase to give unsubstituted fatty amides.[39] More recently Awasthi *et al*. reported the synthesis of fatty amides using urea and di-ammonium hydrogen ortho-phosphate as catalyst in a microwave oven at 200 °C.[40] In 2013, de Almeida *et al*. reported the aminolysis of passion fruit oil with ethanolamine using various heterogeneous catalysts (Fig. 1.13).[41] Best conditions were found to be 3 equivalents of amine and zinc-lanthanum mixed oxide catalyst at 100 °C and achieved full aminolysis in 3 hours.

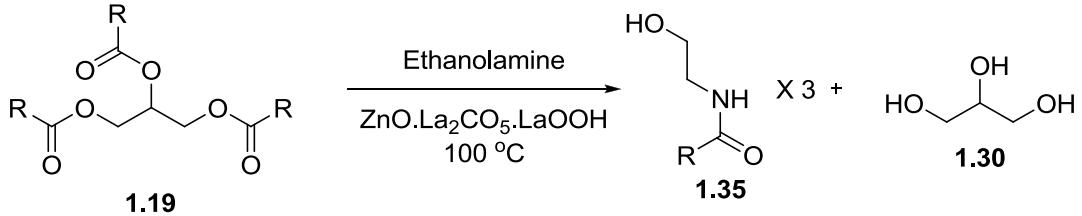


Figure 1.13: Aminolysis of triglyceride using zinc-lanthanum mixed oxide catalyst.

1.4.3 Utilising the Alkene in Triglycerides

1.4.3.1 Hydrogenation

Full removal of the unsaturation present in triglycerides and fatty acids can be achieved *via* hydrogenation. The first reported use on edible oils was in 1902 and is used substantially in the food and chemical industries.[42-44] This process is known as hardening within oil chemistry due to removal of unsaturation within fatty acids increasing their melting points and subsequently altering the physical state of the oil from liquid to semi-solid or solid.[45] Much research has been carried out in this area[46-47] and is achieved using molecular hydrogen and a catalyst, typically nickel,[48] palladium[49-50] or platinum.[51] A standard procedure for the hydrogenation of soybean oil to margarine involves exposing the oil to 55 °C under 300 bar of hydrogen gas in the presence of a nickel based catalyst.[52]

Selective reduction of only one alkene in polyunsaturated fatty acids, such as linoleic acid **1.26** (C18:2), has been reported using palladium on activated carbon (Fig. 1.14).[53] Results showed longer reaction times, when the temperature was maintained at 120 °C and pressure at 0.4 MPa, produced higher amounts of *trans*-fatty acids which have been shown to increase the risk of coronary heart disease.[54]

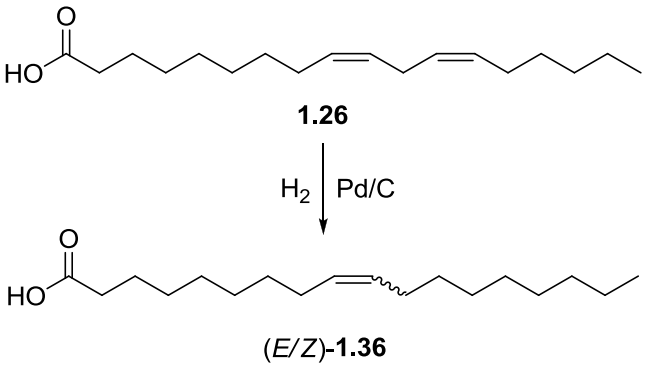


Figure 1.14: Selective hydrogenation of linoleic acid.

1.4.3.2 Direct Cross-linking

In 2001, Li *et al*. discovered triglycerides with high iodine values, a test to determine the amount of unsaturation within a molecule, can be directly polymerised using boron trifluoride diethyl etherate ($BF_3.OEt_2$) as initiator,[55-58] however, due to the higher viscosity of the oil and low miscibility between the oil and initiator, only soft weak polymers or viscous liquids with limited uses were obtained.[55] Addition of more reactive styrene and divinylbenzene co-monomers improved both miscibility and reactivity of the triglyceride reactions and produced polymers with glass transition temperatures of 0 – 105 °C therefore ranging from soft rubbers to hard, tough or brittle plastics.[56-58] Following on from this research in 2007 Liu *et al*. achieved cationic polymerisation using $BF_3.OEt_2$ in supercritical CO_2 and obtained polymers *via* a green method with molecular weights (M_w) ranging from 1300 to 22800 $gmol^{-1}$ which could have potential uses as lubricants and hydraulic fluids due to the liquid physical state.[59]

Triglycerides with high iodine values (> 170) are referred to as drying oils due to their increased ability to polymerise *via* radical polymerisation caused by autoxidation and subsequent peroxide formation.[60-61] The radical process generally starts with the abstraction of a hydrogen atom from the activated methylene between the two *cis* alkenes in the polyunsaturated fatty acid **1.37** (Fig. 1.15) to give a resonance stabilised radical **1.38a** ↔ **1.38b**. This causes conjugation of the double bonds and after reaction with O_2, in the air **1.39**, leads to the formation of hydroperoxide **1.40**. Thermal degradation of the hydroperoxide leads to oligomerisation between the fatty acid chains *via* ether linkages **1.41**. Alkyl

oligomers can be produced if **1.38a** or **1.38b** lead to termination and peroxy oligomers can be produced if **1.39** terminates with **1.38a** or **1.38b**.

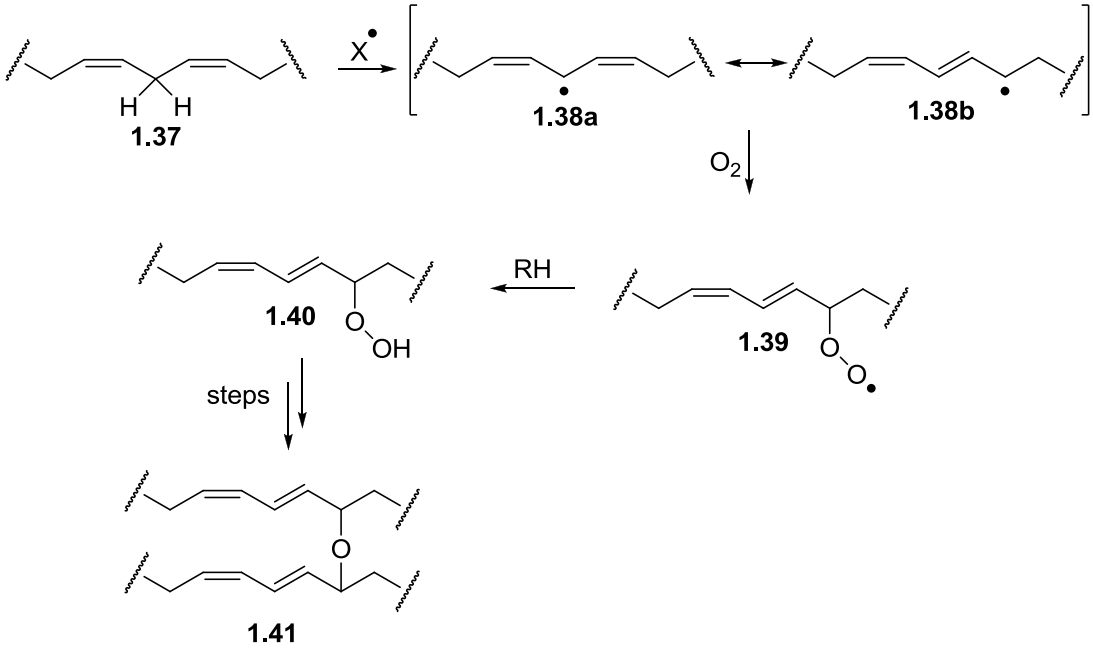


Figure 1.15: Autoxidation in drying oils.[62]

This makes them important compounds for use as binders and film formers in paint and coating formulations. Addition of cobalt, as a drying agent, increases the drying rate without affecting the mechanism, however leads to a solid layer formation on thick films while remaining liquid underneath therefore being one of the major drawbacks of drier use.[62] Cross-linking is achieved when the radicals formed from the autoxidation recombine in various ways to form alkyl, ether or peroxy cross-link bridges.[63-64] Recent work in this area has established the use of manganese compares well to cobalt as a drying agent[65-66] and could therefore be used as non-carcinogenic alternatives.[67]

1.4.3.3 Metathesis

Catalytic metathesis has become a very useful tool in organic and materials chemistry since its discovery by Banks and Bailey in 1964.[68] The first reported use

of metathesis for oleochemicals was the self-metathesis of methyl oleate using a WCl_6/Me_4Sn catalyst system[69] which was followed by using linoleate and linolenate based esters[69-70] however conversions tended to be low with 50 % plus starting material recovered. Since this report, other catalytic systems have been investigated for the self metathesis of fatty acids with alumina supported rhenium oxide (Re_2O_7/Al_2O_3),[71] $Re_2O_7/SiO_2.Al_2O_3/SnBu_4$[72] and subsequently with Grubbs catalysts,[73-74] with all giving higher conversions of dicarboxylic acids **1.43** and alkene **1.44** than with the original tungsten based catalyst (Fig. 1.16).

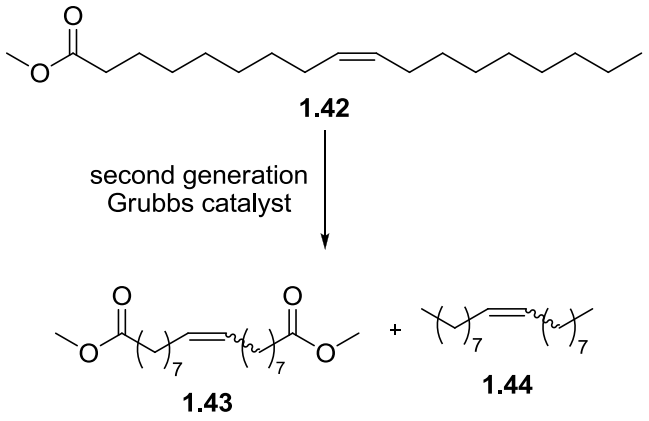


Figure 1.16: Self metathesis of methyl oleate using second generation Grubbs catalyst.[73]

Recently Dixneuf *et al*. synthesised a range of aminoacid, aminoester and aminoalcohol precursors from oleic acid and fatty acids from castor oil (Fig. 1.17).[75] Fatty acids and diacids **1.43** were cross metathesised with acrylonitrile **1.46** and fumaronitrile to prepare various nitrile-acids and nitrile-esters which could be further reduced using the residual metathesis catalyst giving the aminoacids, aminoesters **1.48** and aminoalcohols which have potential as polyamide monomers and as renewable intermediates in the chemical industry.[76]

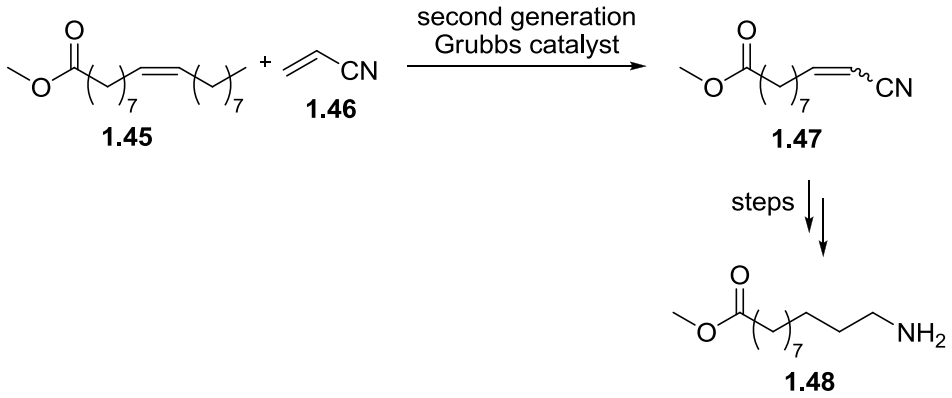


Figure 1.17: Synthesis of aminoesters from castor oil fatty acids.

In 1990 Wagener *et al.* demonstrated the polymerisation of α,ω-dienes and coined the term acyclic diene metathesis (ADMET) polymersisation.[77] ADMET is a step growth polymerisation driven by the release of ethane as condensate and typically yields linear polymers with unsaturated backbones (Fig. 1.18).[78]

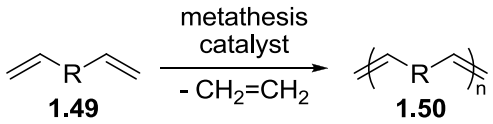
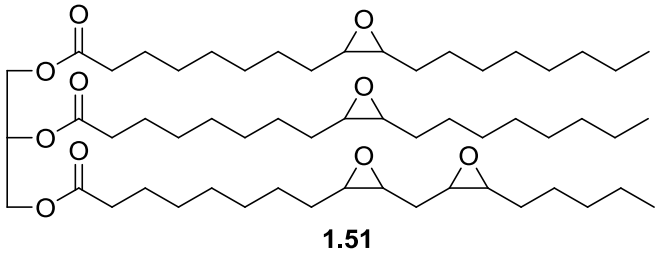


Figure 1.18: Schematic representation of an ADMET polymerisation of α,ω-dienes.[78-79]

In 2002, Larock *et al*. carried out ADMET polymerisation using soybean oil.[80] the polymers produced ranged from sticky oils to rubbery materials depending on the conditions used. Following on from this, in 2010 Meier *et al*. successfully achieved a similar acyclic triene metathesis (ATMET) polymerisation using high oleic sunflower oil with differing ratios of methyl acrylate chain stopper.[81] Varying the chain stopper varied the molecular weight of the polymer with lower amounts of chain stopper leading to larger molecular weights.

1.4.3.4 Epoxidation

One of the most important reactions with regards to oil chemistry is the epoxidation of the unsaturation within the fatty acid chains of triglycerides (Fig. 1.19). This modification gives rise to a range of possibilities to add further functionalisation to the triglycerides for many different purposes.



1.51

Figure 1.19: Epoxidised rapeseed oil.

There are many methods of epoxidation, one of the most common is the use of peroxide containing compounds (peracids) such as mCPBA, known as the Prilezhaev reaction,[82-83] however this process would not be viable commercially due to the benzoic acid by product produced and the cost implications of using mCPBA. Interestingly in 1996 Klaas *et al*. discovered a one-pot peracid formation/epoxidation using unsaturated fatty acids.[84] Oleic acid **1.22** was oxidised to peroxy oleic acid **1.44** using 35 % hydrogen peroxide (H_2O_2) and lipase enzyme from *Candida antarctica* at 40 °C. Peroxy oleic acid **1.52** is present only as an intermediate before epoxidation of the unsaturation within the fatty acid chain to form epoxidised oleic acid **1.53** (Fig. 1.20). As lipase enzymes cause hydrolysis of triglyceride esters, the group successfully achieved the epoxidation of rapeseed oil and linseed oil using lipase and H_2O_2. This process however, leads to the formation of mono- and di-glycerides so the group added 5 % free fatty acid, of the same composition and origin as the oil, to successfully prevent the hydrolysis of the triglyceride.

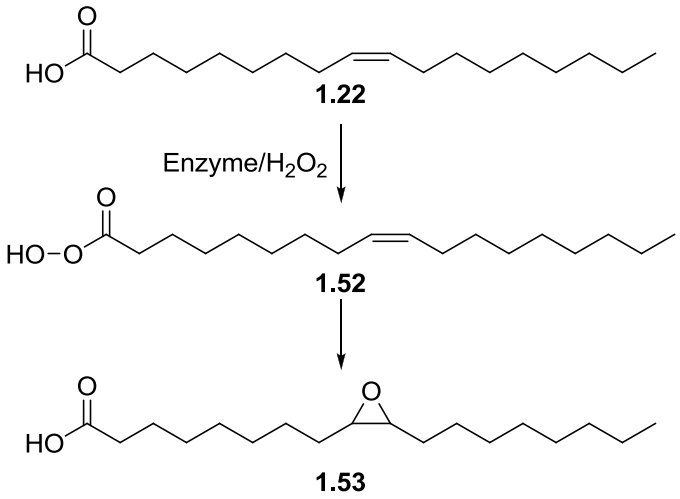


Figure 1.20: Peracid formation and subsequent epoxidation of oleic acid 1.22.

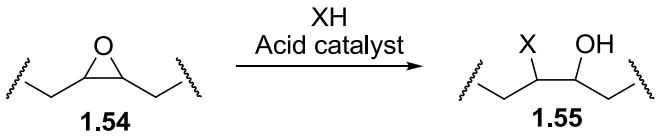
Following on from this, in 2001, Hilker *et al*. successfully epoxidised linseed oil using peroxy stearic acid (saturated fatty acid) using the same process as Klaas *et al*. and discovered the rate of reaction varied with the temperature of the reaction and the H_2O_2 percentage. It was found that increasing the temperature increased the rate of reaction however also lead to decomposition of the peracid and deactivation of the enzyme.[85] Industrial epoxidation is achieved using the Cargill process where peracetic acid is formed *in situ* (from acetic acid and H_2O_2) or formed externally and added to the reaction.[86-87]

Many catalytic methods of epoxidation involve transition metal complexes, using Ti, Cr, Mo, Re or W, and H_2O_2 as oxidant.[88-90] Du *et al*. studied the effects of catalyst amount on the epoxidation of methyl linoleate using methyltrioxorhenium (MTO) with pyridine and H_2O_2 and found catalyst loadings could be lowered to 1 mol % and still reach full epoxidation with increased reaction times.[88] Gerbase *et al*. used a biphasic system, MTO-CH_2Cl_2/H_2O_2, to fully epoxidise soybean oil in 2 hours.[91] Lowering the catalyst and/or H_2O_2 amounts allows oils with desired epoxide content to be synthesised. Crivello *et al*. attempted the epoxidation of triglyceride oils using

two methods, the first using peracetic acid, prepared externally and added to the reaction, and secondly using peroxotungstate catalyst and H_2O_2 and found both gave the desired epoxidised oil at 55 – 60 °C in 8 and 9 hours respectively.[92] Crivello prepared the peracetic acid using Amberlite® IR 120 ion exchange resin, acetic acid and H_2O_2, in 2002 Petrovic *et al.* used a similar system to epoxidise soybean oil producing the peracetic acid *in situ* in toluene at 40 – 80 °C and found increased temperatures decreased reaction times without compromising conversion.[93]

1.4.3.5 Ring-opening of epoxides

Epoxides are relatively strained species and as a result are more reactive. Epoxides tend to undergo nucleophilic ring-opening usually to form alcohol derivatives (**1.55a-h**) (Fig. 1.21). These alcohol derivatives give rise to compounds that can be used as monomers in polyurethane synthesis (see section 2.1) or further modified *via* nucleophilic substitution of the β-hydroxy halo triglycerides (**1.55e-f**).[94-95]



x = (**a**) OH, (**b**) OR, (**c**) NR_2, (**d**) SR, (**e**) Br, (**f**) Cl, (**g**) N_3, (**h**) H

Figure 1.21: Nucleophilic ring-opening of epoxides.

1.4.3.6 Dihydroxylation

Direct dihydroxylation of alkenes is an extremely useful transformation for fatty acids to produce polyols. The use of high oxidation state osmium and ruthenium based catalysts are most common in direct dihydroxylation with Sharpless asymmetric dihydroxylation being one of the key reactions.[96-99] Potassium

permanganate can also be used for direct dihydroxylation with sodium hydroxide and phase transfer catalyst however, reactions with methyl oleate were poor due to potential saponification caused by the presence of NaOH in the reaction (Fig. 1.22).[100]

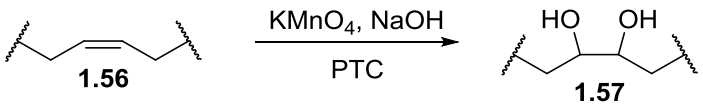


Figure 1.22: Direct dihydroxylation using potassium permanganate.[100]

Dihydroxylation has also been reported *via* epoxide intermediates. Oakley *et al*. demonstrated the one-pot epoxidation and subsequent ring-opening of fatty acids using H_2WO_4 as a catalyst with *t*-butanol, H_2O_2 and O_2. This method could also be used to produce dicarboxylic acids *via* oxidative cleavage if further equivalents of O_2 or H_2O_2 were used.[101] In 2003 Usui *et al*. reported the use of 30 % H_2O_2 with resin-supported sulfuric acid to dihydroxylate oleic acid as well as other olefins (Fig. 1.23).[102]

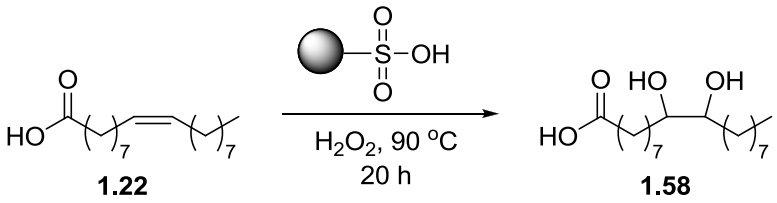


Figure 1.23: Dihydroxylation of oleic acid using resin-supported sulfuric acid.[102]

Two years later Okieiman *et al*. reported a one-pot epoxidation dihydroxylation of rubber seed oil using formic acid and H_2O_2 to produce peroxyformic acid *in situ*.[103] Epoxidation was achieved at 60 °C in 8 hours when the temperature was raised to 80 °C for another 14 hours to produce dihydroxylated rubber seed oil.

1.4.3.7 Thiol-ene reaction

The thiol-ene reaction is often referred to as an example of 'click chemistry' which was first reported by Sharpless *et al.*[104-105] A more detailed description of click chemistry is given in section 1.5. The thiol-ene reaction has been successfully employed in the synthesis of polyols from fatty acids and triglycerides.[106] Methyl oleate was reacted with 2-mercaptoethanol using dimethoxy-2-phenylacetophenone (DMPA) as a photo initiator under UV conditions to give hydroxylated methyl oleate **1.59** as a mixture of regioisomers (Fig. 1.24).

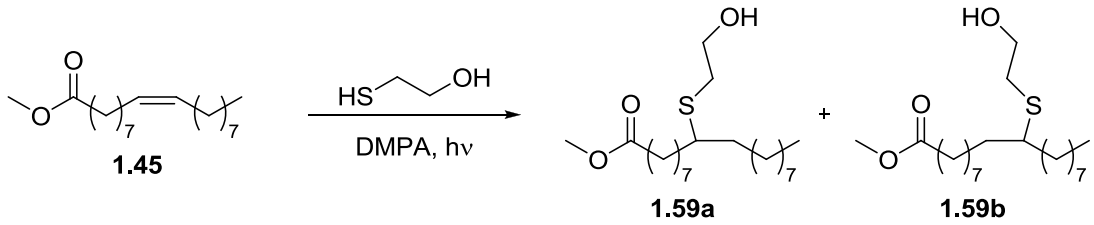


Figure 1.24: Thiol-ene reaction of methyl oleate with 2-mercaptoethanol.

Reduction of **1.59** with $LiAlH_4$ leads to diol **1.60** which has been used in the synthesis of polyurethanes (Fig. 1.25).[106]

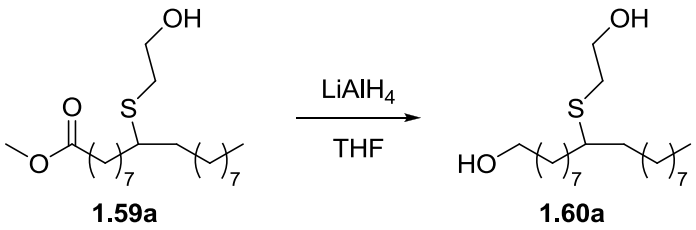


Figure 1.25: Reduction of 1.59a with $LiAlH_4$ to give diol 1.60a.

In 2011 Desroches *et al*. reported thiol-ene click using rapeseed oil and 2-mercaptoethanol without photoinitiation, the products were subsequently

polymerised with 4,4′-methylenebis(phenyl isocyanate) (MDI) to give polyurethanes with glass transition temperatures of 25 °C.[107]

1.4.4 Polymers from epoxidised and dihydroxylated vegetable oil

Polyethers, polyesters and polyurethanes are primarily made by chemical manipulations of various petrochemicals. Replacing the aliphatic chain with one derived from a vegetable oil (e.g. the fatty acid chains in the triglycerides) may show similar properties to those derived from existing monomers. Epoxidised and dihydroxylated vegetable oils can be used to produce polyethers, polyesters and polyurethanes (Fig. 1.26), a brief review has been given below.

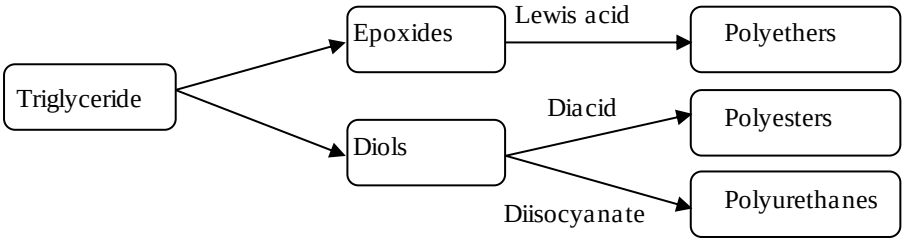


Figure 1.26: Schematic representation of the polymerisations and monomers.

1.4.4.1 Polyethers

Ring-opening of epoxides using Lewis acids leads to polyethers which can also be further polymerised with isocyanates to give polyurethanes.[108-112] In 2006 Lligadas *et al*. ring-opened epoxidised methyl oleate **1.61** using hexafluoroantimonic acid ($HSbF_6$) to give methyl oleate based polyethers **1.62** which were further reduced using $LiAlH_4$ to give polyethers with increased hydroxyl values **1.63** (Fig. 1.27).[108] These polyols were subsequently reacted with MDI to form polyurethanes ranging from hard rubbers to rigid plastics.

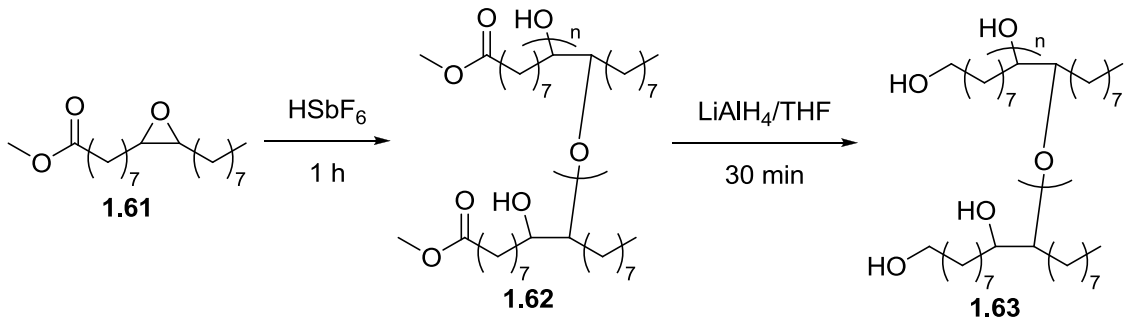


Figure 1.27: Ring-opening polymerisation and reduction of epoxidised methyl oleate.[108]

Following on from this, the same group reported ionic-coordinative ring-opening polymerisation of epoxidised methyl oleate to produce polyethers ranging from 6000 – 8000 molecular weight.[109] These polyethers were subsequently reduced using $LiAlH_4$ to give polyether polyols which were converted to biobased polyether polyurethanes exhibiting increasing tensile strength with increasing cross-linking.[110]

Liu *et al*. reported the ring-opening polymerisation of epoxidised soybean oil using boron trifluoride diethyl etherate as catalyst in DCM in 3 hours at 0 °C.[111] Polyethers produced ranged from 1600 – 3800 molecular weights with glass transition temperatures ranging from -48 – -16 °C depending on the amounts of catalyst. The resulting cross-linked polymers could be converted into hydrogels by chemical modification and could potentially be used in personal care and health care areas.

More recently Clark *et al*. reported the ring-opening polymerisation of epoxidised vegetable oils in THF to produce THF-vegetable oil copolyethers (Fig. 1.28).[112] Epoxidised methyl oleate, cocoa butter and palm oil were used as monomers and produced polyethers ranging from 8000 – 56000 molecular weights depending on the monomer used, palm oil generally giving larger molecular weights due to higher

epoxide count. Polyurethanes were produced from vegetable oil polyethers and THF-vegetable oil copolyethers with the copolyethers showing superior mechanical properties with little effect on thermal stability.

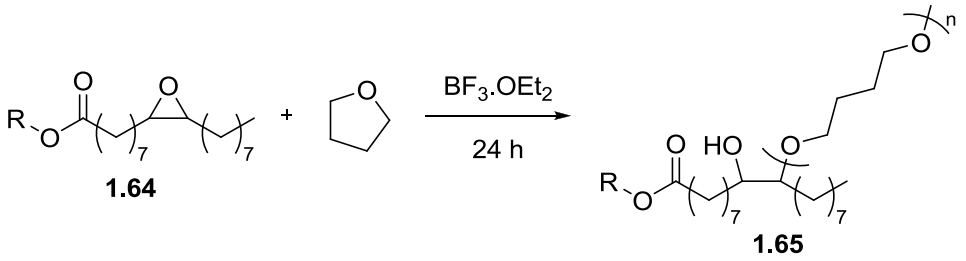
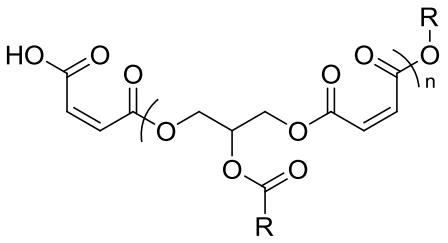


Figure 1.28: Copolymerisation of vegetable oil with THF.[112]

1.4.4.2 Polyesters

The most common use of vegetable oil based polyesters is as alkyd resins in the coatings industry as architectural coatings, industrial product finishes, traffic paints and high gloss offset printing inks.[113] Alkyd resins are comprised of polyhydroxy acids and polybasic alcohols. In a lot of cases these coatings can be modified with fatty acids and monoglycerides derived from the alcoholysis of vegetable oils. Alkyds are predominantly synthesised *via* condensation polymerisation reactions of acids and alcohols producing highly branched polymers with polyester linkages (Fig. 1.29).[114] Cross-linking of the alkyd chains occurs during the curing of the alkyd resins when applied as coatings and is believed to be *via* autoxidation (see section 1.4.3.2),[114] and oils with higher iodine values, drying and semi-drying oils, often have better drying times due to higher linoleic acid moiety therefore more chance to autoxidise and cross-link. Alternatively cross-linking can be achieved using residual hydroxyl groups within the polyester backbone however higher drying temperatures are required, typically 80 – 200 °C.



1.66

Figure 1.29: Alkyd resin structure made from monoglyceride and maleic anhydride.

Aydin *et al*. determined the effects of various anhydrides (maleic anhydride, phthalic anhydride, glutaric anhydride and succinic anhydride) on alkyd film viscosities and properties.[115] Two different methods of alkyd resin synthesis were tested; the conventional method, alcoholysis of triglyceride and subsequent reaction with anhydride, and a modified method where partial glycerides, mono- and di-glycerides, were synthesised and washed with water to remove excess glycerol before reaction with anhydrides. Removal of the excess glycerol lead to alkyds with better film properties and lower viscosities.

1.4.4.3 Polyurethanes

Polyurethanes (PU) are commonly synthesised from polyols and diisocyanates such as hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (TDI) or 4,4'-methylene bis(phenylisocyanate) **1.67** (MDI) (Fig. 1.30). Structurally a PU can be separated into two components, a hard segment, typically formed from the urethane link (Fig. 1.30), and a soft segment, typically made from the polyol and this component normally imparts flexibility in the polymer. Flexible materials are usually made from large polyols, molecular weight typically 3000-6000, containing low hydroxyl groups, typically 2-3, leading to low cross-linking densities and

flexible structures. Lowering molecular weight and increasing hydroxyl groups increase the rigidity and cross-linking densities of the PUs.

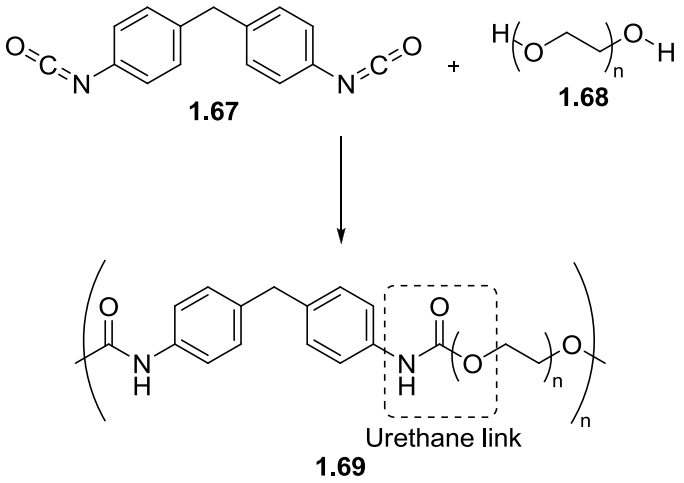
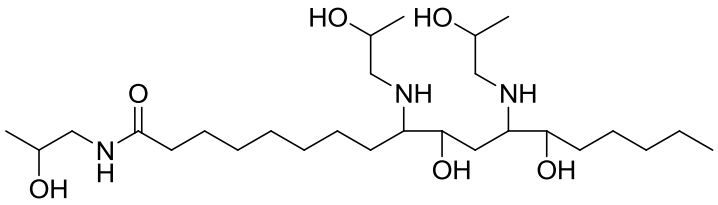


Figure 1.30: Synthesis of polyurethanes from MDI and PEG polyol, showing urethane link.

A vast amount of research using vegetable oils for polyurethane synthesis has been reported. Epoxides ring-opened with various reagents to form short polyols or longer chained polyols and polyamines have been employed. Petrovic *et al*. have carried out studies on the use of polyols derived from soybean oil for the use in polyurethanes[83,95,116-118] and more details are given in the introduction to chapter 2 (section 2.1).

Wang *et al*. synthesised polyurethanes from methanol, ethylene glycol and 1,2-propanediol ring-opened epoxidised soybean oil **1.55b** (Scheme 1.21). Results showed tensile strength of the PUs increased with increasing hydroxyl value however, thermal stability and elongation decreased due to increased cross-linking.[119] Miao *et al*. reported bio-based polyurethanes from epoxidised soybean oil and isopropanolamine where both the ester and epoxide groups were reacted with the amine to generate polyols **1.70** (Fig. 1.31) with differing amounts of isopropanolamine. Unreacted epoxides were subsequently ring opened with HCl to

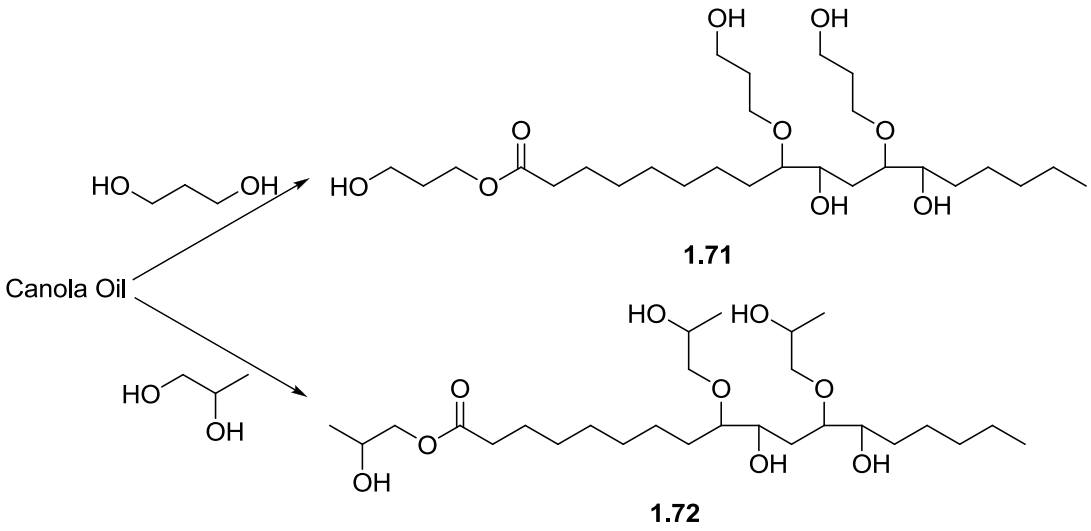
increase hydroxyl numbers. Polyurethanes produced had tensile strengths ranging from 2.74 MPa to 27.76 MPa depending on the amounts of isopropanolamine used to prepare the monomers, with the higher amounts giving the higher strengths.



1.70

Figure 1.31: Monomer produced by Miao *et al*. for bio-based polyurethanes.[120]

Kong *et al*. produced polyurethanes from monomers derived from canola oil using 1,2- and 1,3-propanediol (Fig. 1.32) to produce poly(ether ester) polyols **1.71** (1,3-propanediol) and **1.72** (1,2-propanediol).[121] Polyurethanes synthesised from **1.71** were shown to have better initial thermal properties and shorter gelation times however, those prepared from **1.72** have better middle stage thermal properties and higher glass transition temperatures.

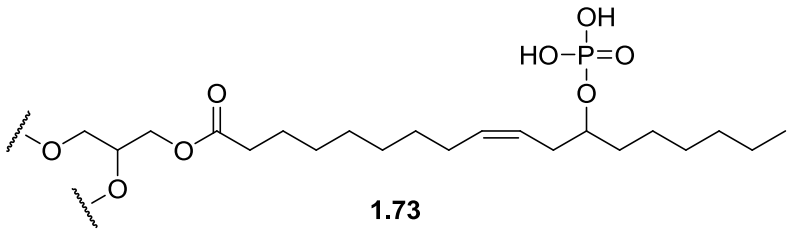


1.71

1.72

Figure 1.32: Poly(ether ester) polyol monomers derived from canola oil.[121]

Soybean oil and sunflower oil polyurethanes were investigated for tissue engineering and showed promising cell adherence and proliferation.[122-123] Cell adhesion of fatty acid derived polyurethanes has been improved by blending or surface modification of polyurethanes with gelatin,[124] chondroitin sulfate[125] and collagen.[126] The problem encountered by these materials was the non-degradable urethane links. Very recently a series of biodegradable and biocompatible phosphoester cross-linked vegetable oil polymers were reported.[127] Phosphorylated castor oil **1.73** (Fig. 1.33) was reacted with epoxidised linseed oil to produce the phosphoester cross-linked vegetable oil elastomers showing full degradation and complete absorption after 3 months with very slight inflammatory response.



1.73

Figure 1.33: Phosphorylated castor oil.

1.5 Click Chemistry

As previously mentioned (section 1.4.3.7) Sharpless first coined the term ‘click chemistry’ in 1998, however it was not fully described until 2001.[104] In order to be classed as ‘click,’ reactions have to be:

- Modular
- Wide in scope
- High yielding
- Generate inoffensive by-products

- Stereospecific (not necessarily enantioselective)
- Simple reaction conditions
- Use of benign or no solvent
- Simple purification

There are 4 main areas that have been studied as click reactions: cycloaddition reactions, nucleophilic ring-opening reactions, non-aldol carbonyl chemistry and addition to C=C bonds.[128]

1.5.1 Azide-alkyne cycloadditions

The best example of click chemistry is the Huisgen 1,3-dipolar cycloaddition of alkynes and azides producing triazoles.[129] This process has been used in the production of small molecules and potential drug discovery[128] however medicinal chemists have not given this area much interest potentially due to the use of azides.[130-131] Most azide alkyne cycloadditions are catalysted by copper (II) salts and base producing the active copper (I) catalyst *in situ*. This leads to 1,4-disubstituted triazoles due to the terminal copper acetylide formed during the reaction, however reactions can be carried out catalyst free which leads to formation of a small percentage (~ 20 %) the minor product, 1,5-disubstituted triazoles.[132]

Azide-alkyne click chemistry has been used in the synthesis of polymers since 2004 when Scheel *et al*. synthesised hyperbranched poly(triazoles) incorporating both azide and alkyne functional groups within one molecule (see section 4.1 for more details).[133] Since this work most poly(triazoles) are synthesised using dialkyne and diazide units and has been reviewed extensively (Fig. 1.34).[134-136]

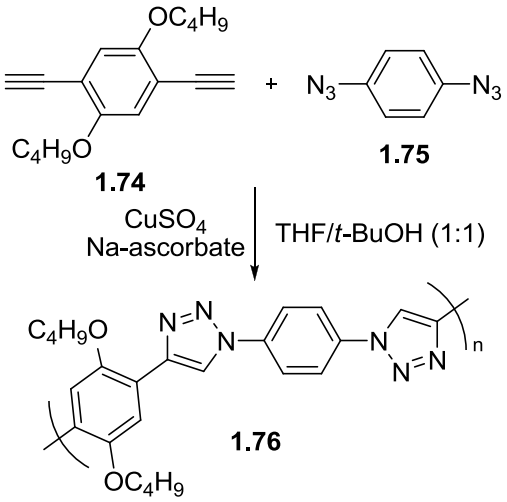


Figure 1.34: Example of azide-alkyne click polymerisation.[137]

The use of azide-alkyne click chemistry using vegetable oils is a relatively new and uninvestigated area. In 2010 Shah *et al*. attempted azide-alkyne click polymerisation using soybean oil[138] and expanded to other oils in 2012.[139] The work by Shah *et al*. is discussed in more detail in the introduction to Chapter 3.

1.5.2 Nitrile oxide-alkyne cycloadditions

Nitrile oxide-alkyne cycloadditions are seen as an alternative to azide-alkyne cycloadditions for two reasons, firstly toxicity of copper salts[140] and secondly the instability and risk to health aspects of azides.[141] Nitrile oxide dipoles are potentially unstable, forming dimers (Fig. 1.35)[142] or reacting with nucleophiles however, this can be minimised by *in situ* generation of the dipole.[143]

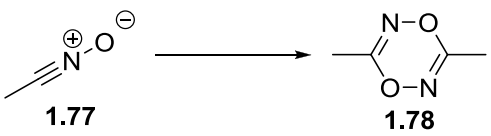


Figure 1.35: Dimerisation of nitrile oxides to 1,4,2,5-dioxadiazines.

Nitrile oxide dipoles can be formed from either hydroxymoyl chlorides with base or from nitro precursors in the presence of isocyanates[144] and lead regioselectivly to 3,5-disubstituted isoxazoles **1.80** when reacted with monosubstituted alkynes **1.79**.[145] The regioisomeric 3,4-disubstituted isoxazoles can be produced in the presence of ruthenium based catalysts,[146] while copper based catalysts give the 3,5-disubstituted isoxazoles.[147]

Nitrile oxide cycloadditions with terminal alkynes has been used to synthesise steroids and sugar conjugates (Fig. 1.36)[148-150] however, the field is dominated by the antiviral and anticancer potential of isoxazole nucleosides.[145,151-152]

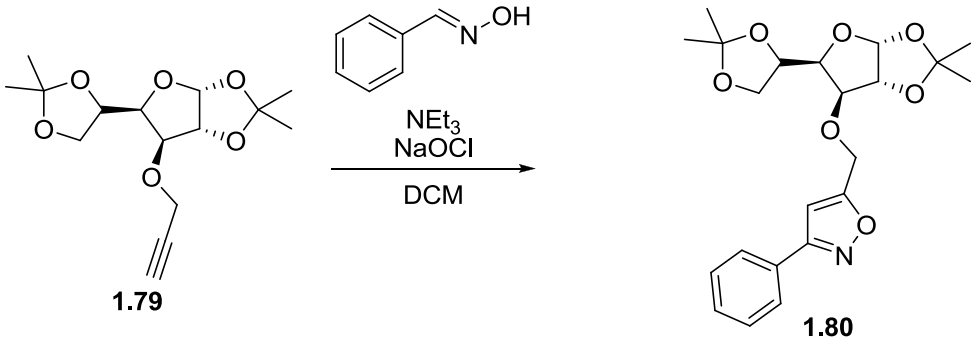


Figure 1.36: Synthesis of isoxazole conjugates of sugars.[149]

The use of nitrile oxide cycloadditions in polymer chemistry is a relatively new area. Takata *et al*. synthesised a range of polymers using dialkyne and dinitrile oxide precursor units and tested a range of conditions,[153-154] more details of the work by Takata *et al*. is given in the introduction to Chapter 5. Nitrile oxide cycloadditions have been used in post polymerisation modifications to impart potential bioactivity due to the isoxazole moiety (Fig. 1.37).[155]

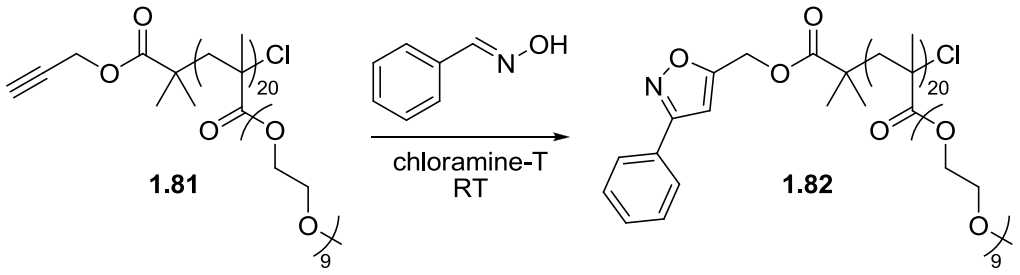


Figure 1.37: Post polymerisation chain end modification using nitrile oxide cycloaddition.[155]

To the best of our knowledge the use of vegetable oil derived monomers in nitrile oxide polymerisations has not been studied and therefore this gives a new area to investigate.

2.0 Wealth out of waste: Synthesis of Polyurethanes from Waste Cocoa Butter

2.1 Introduction

In 2000 Petrovic *et al*. synthesised polyurethanes from halogenated and non-halogenated soybean oil.[94] Epoxidised soybean oil **2.1** was ring-opened with methanol, hydrochloric acid, hydrobromic acid or hydrogen (Fig. 2.1) giving monomers with a range of hydroxyl values (Table 2.1).

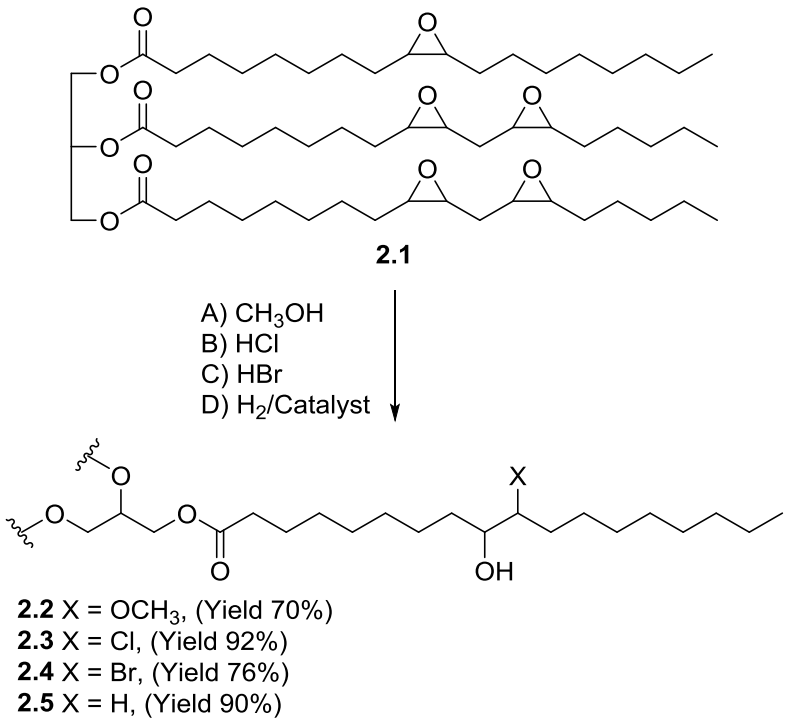


Figure 2.1: Halogenated and non-halogenated ring-opened soybean oil 2.2-2.5.

Polyol	Conversion (%)	Hydroxyl value	Functionality
Soy-OCH_3 **2.2**	93	199	3.7
Soy-Cl[a] **2.3**	94	192	3.8
Soy-Br[a] **2.4**	100	182	4.1
Soy-H **2.5**	89	212	3.5

[a] All values were calculated on the basis of the analyzed Cl and Br contents and under the assumption that each halogen was accompanied by a hydroxy group.

Table 2.1: Properties of soybean oil derived polyols 2.2-2.5.

Polyols **2.2-2.5** were subsequently polymerised using two isocyanates, PAPI 2901 (a crude MDI, MDI = 4,4'-methylenebis(phenylisocyanate)) and Isonate 2143L (a liquid MDI prepolymer containing carbodiimide bonds) (Fig. 2.2).[95] Polymers exhibited high T_g values (above RT) and gave relatively high tensile strength materials with low elongation at break (Table 2.2).

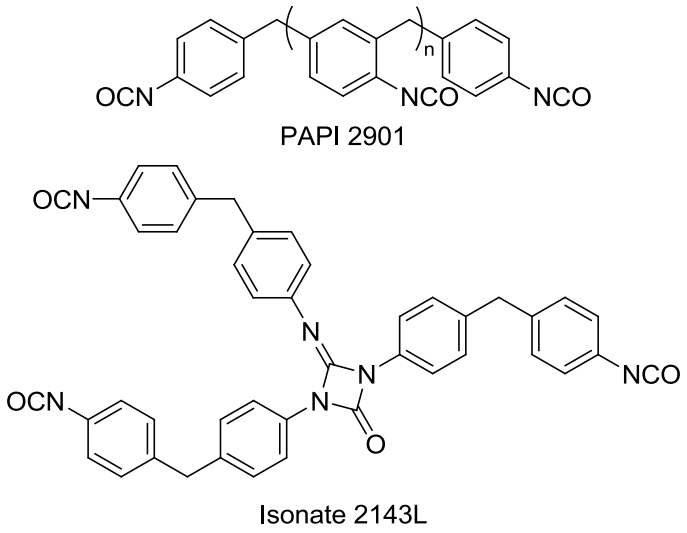


Figure 2.2: Structures of PAPI 2901 and Isonate 2143L.

Polyol	T_g[a] (°C)		TS (MPa)		Elongation (%)		YM(MPa)	
	PAPI	Isonate	PAPI	Isonate	PAPI	Isonate	PAPI	Isonate
Soy-Met **2.2**	72	70	45	46	8.4	9	986	979
Soy-Cl **2.3**	77	73	48	46	7.5	8.9	1204	1190
Soy-Br **2.4**	75	68	44	40	7.7	7.3	1102	955
Soy-H2 **2.5**	31	34	19	16	29.0	15.4	383	362

[a] T_g determined by DSC. TS = tensile strength, YM = Young's Modulus

Table 2.2: Physical properties comparison of soybean oil polyols polyurethanes.

In 2004 Petrovic *et al.* synthesised six polyurethanes from polyols derived from canola, midoleic sunflower, soybean, linseed, sunflower and corn oils.[156] The aim was to identify the effect different triglyceride structures had on the properties of any subsequent MDI derived polyurethanes. The group found that while the position of

the reactive sites (Fig. 2.3) in the polyurethanes had little effect on the properties, the cross-linking densities were more important. As expected, higher cross-linking densities gave superior mechanical properties with higher T_g's (Table 2.3). Mobility of the chains in the networks was inversely proportional to the cross-linking density.

Polyol	T_g [a] (°C)	TS (MPa)	Elongation (%)	FM (MPa)
Canola	32	22.9	131	353
Midoleic Sunflower	24	14.8	168	10
Soybean	31	20.2	108	312
Linseed	77	56.3	8	2015
Sunflower	32	21.7	107	443
Corn	30	17.7	122	309

[a] T_g determined by DSC. TS = tensile strength, FM = Flexural Modulus

Table 2.3: Physical properties of 6 renewable polyurethanes derived from different polyols.

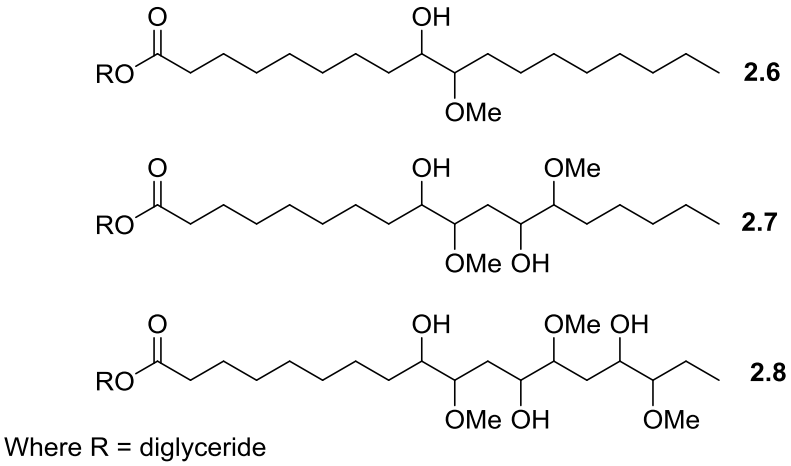


Figure 2.3: Reactive sites on different fatty acid chains of triglycerides.

In 2008, Coles *et al*. synthesised six polyurethane samples, three from, HEMP (hempseed oil), HEAR (high erucic acid rapeseed oil) and rapeseed oil with varying fatty acid compositions and three synthetic mimics of the oils (prepared from glycerol and fatty acids) with similar fatty acid profiles in order to establish whether

polymers from natural oils could be mimicked synthetically in the lab.[157] Functionalisation of the oils was achieved *via* hydroxylation of the double bonds using peroxotungstate catalyst (Fig. 2.4).[89]

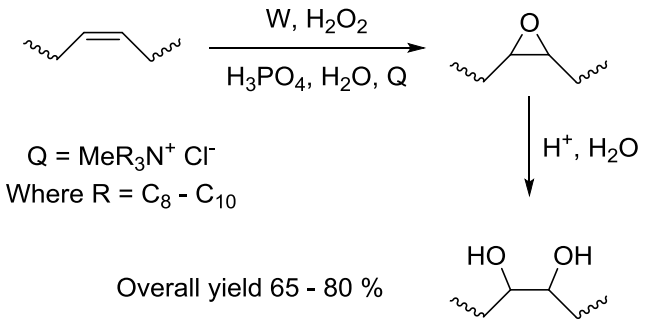


Figure 2.4: Schematic representation of hydroxylation reaction using tungsten.

Subsequent polymerisation with MDI also showed the polymers were sensitive to subtle changes in fatty acid composition. It also concluded that synthetic mimics of natural triglyceride based polyurethanes could be prepared and that these have similar properties to the natural oil polymers. This is useful when only small quantities of novel natural oils are available as it allows it to be mimicked in the lab on a larger scale.

In recent years, vegetable oils from renewable sources have proved useful monomers for polymer synthesis in industry. The two most common vegetable oils used industrially, soybean and palm oil, are now deemed to be environmentally unfriendly due to i) the subsequent loss of agricultural land for food use or ii) the large amounts of deforestation required for plantations and therefore loss of ecosystems and increase in greenhouse gas emissions.[158-161] As a result of this, alternative sources of renewable triglycerides are required, preferably from waste industrial processes. Cocoa butter **2.9** (Fig. 2.6) is a triglyceride extracted from

cocoa beans and is comprised of 64 % saturated and 36 % unsaturated fatty acids (Table 2.4). Cocoa beans are harvested, roasted and then ground into a cocoa liquor. This liquor is then pressed to yield the cocoa butter and cocoa mass. The global production of grinds from cocoa beans in 2012/13 was 4.1 million tonnes with estimates for this year to be 4.2 million tonnes.[162] The amount of cocoa butter extracted from the cocoa liquor is 54 % therefore last year's production of cocoa butter was 2.2 million tonnes.[163] Cocoa butter is primarily used in the confectionary industry and makes up approximately 20 % of chocolate.[164] It is expected in 2014 the global consumption of chocolate to be 7.3 million tonnes therefore, as cocoa butter makes up on average 20 % of chocolate, 1.46 million tonnes of cocoa butter is required. Some of the remaining cocoa butter is used in the production of body lotions and suppositories by pharmaceutical companies, however a significant amount is discarded as waste. Consequently, it is an ideal candidate as a feedstock to make polymeric materials. The triglyceride structure (Fig. 2.6) is heavily saturated; with on average one oleic acid residue per triglyceride. Titrations were carried out to further corroborate the amount of unsaturation and free fatty acid within the cocoa butter starting material, results gave iodine values of 35 showing on average one double bond per molecule. Acid value titrations gave values of 10 which show a presence of 4 % free fatty acid within the starting material. This was also confirmed with GPC analysis of the cocoa butter monomer where a small percentage of free fatty acid can be observed in the GPC trace (Fig. 2.5) at retention times indicative of pure palmitic, stearic or oleic acid samples.

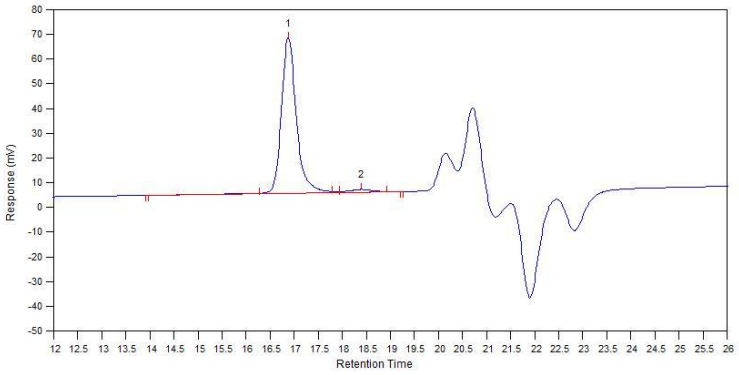
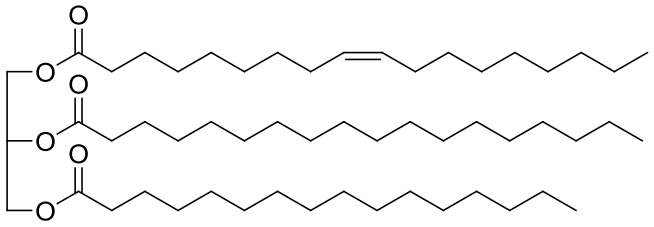


Figure 2.5: GPC trace of cocoa butter starting material.



2.9

Figure 2.6: Structure of cocoa butter triglyceride.

Fatty acid	Cocoa butter (%[a])	Palm oil (%[a])
Palmitic acid (C16:0)	26	42
Stearic acid (C18:0)	38	4
Oleic acid (C18:1)	32	43
Linoleic acid (C18:2)	3	10
Arachidic acid (C20:0)	1	1

[a] Fatty acid composition determined by FAME analysis

Table 2.4: Fatty acid composition of cocoa butter compared to palm oil.

2.2 Aims and objectives

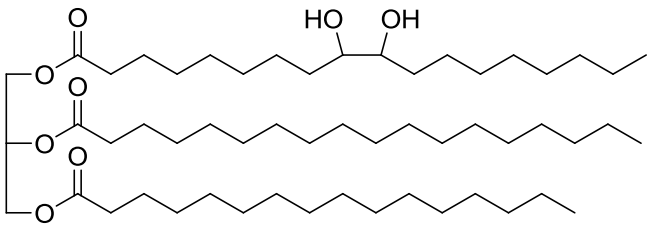
- Investigate the epoxidation / hydroxylation reaction of cocoa butter and determine the physical properties of the derived polyols.

- Prepare MDI derived polyurethanes from cocoa butter polyols and compare their physical properties to those synthesised from other triglycerides.
- Incorporate food-safe dyes into the polyurethanes and assess their stability.

2.3 Ring-opened cocoa butter synthesis

2.3.1 Optimising the ring-opening of epoxidised cocoa butter

In order to synthesise polyurethanes derived from cocoa butter, hydroxylation of the unsaturation in the triglyceride was required. This was first attempted using the procedure employed by Coles *et al*. where a one-pot epoxidation followed by ring-opening was achieved using a peroxotungstate catalyst, hydrogen peroxide and ortho-phosphoric acid (1 equiv. per double bond) in water with a phase transfer catalyst at 100 °C, (Fig. 2.7).



2.10

Figure 2.7: Hydroxylated cocoa butter 2.5.

Although this gave a crude polyol **2.10** in 99 % yield, analysis indicated that hydroxylation was also accompanied by 25 % hydrolysis of the triglyceride to give a mixture of tri-, di- and mono- glycerides, as well as free fatty acids. Acid value titrations gave values of 59 which show a presence of 25 % free fatty acid within crude **2.10**. This was also confirmed with GPC analysis where a larger percentage of

free fatty acid can be observed along with mono- and di-glyceride when compared to the starting material (Fig 2.8). Hydroxyl values confirm full ring opening of the epoxide with values of 77. Mass spectrum of 2.10(25%) shows the non-selectivity of the hydrolysis as all three possible diglycerides are present.

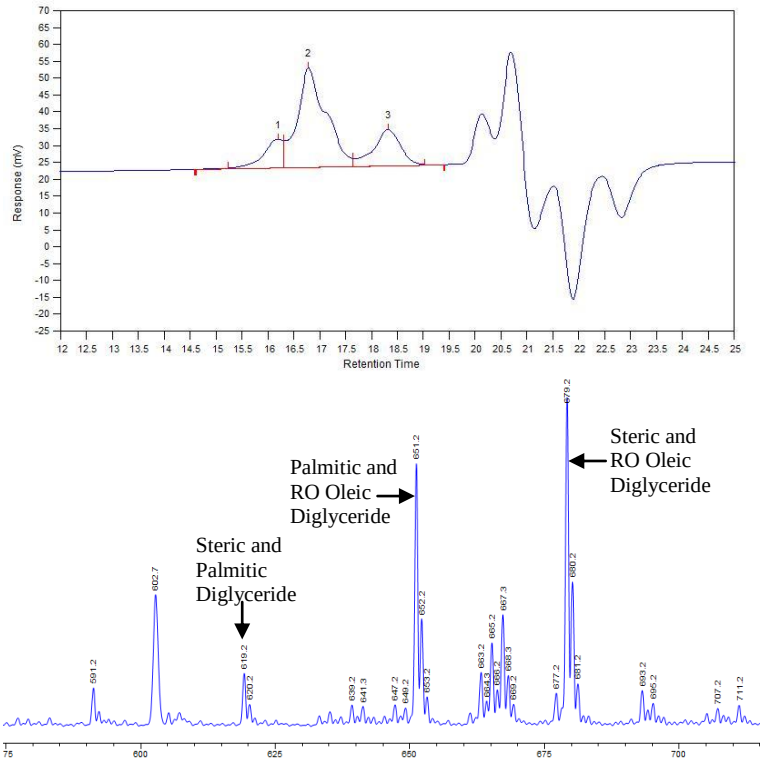
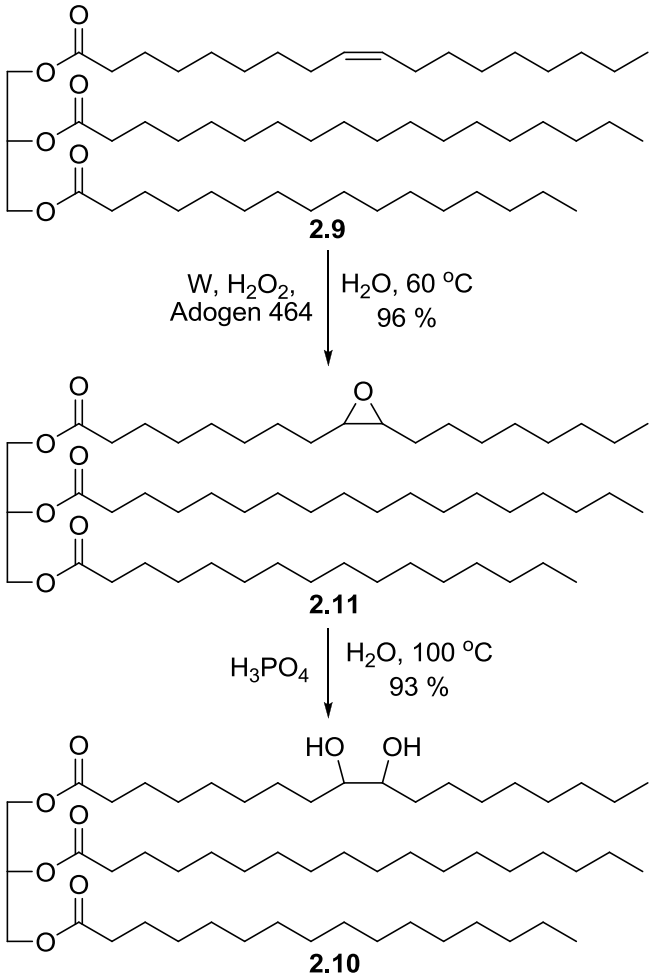


Figure 2.8: GPC trace and mass spectrum of 25 % hydrolysed crude 2.10.

In order to determine if the amount of hydrolysis could be reduced and assess what conditions were responsible for it the process was modified into a two-step procedure with separation of the epoxidation from the ring-opening stage. First, epoxidation was achieved using the peroxotungstate catalyst, hydrogen peroxide and phase transfer catalyst (adogen 464), at the lower temperature of 60 °C for 6 hours. The crude mixture was washed with water to give the fully epoxidised cocoa butter **2.11** in 96 % yield without any evidence of hydrolysis, (Scheme 2.1). Subsequent ring-opening was investigated using ortho-phosphoric acid in water at 100 °C for 24

hours. This gave desired polyol **2.10** in 93 % yield, along with 20 % hydrolysis of the triglyceride, (Scheme 2.1). This confirmed that the second acidic ring-opening step was responsible for the hydrolysis.



Scheme 2.1: Epoxidation and ring-opening of cocoa butter.

While it was not possible to vary the temperature of the second stage (ring-opening didn't occur at lower temperatures), it was possible to alter the amount of acid used. Test reactions were attempted on a 5 g scale, using 1.2 and 0.8 equivalents of 1M H_3PO_4 with respect to the cocoa butter (Table 2.5).

Entry	H_3PO_4[a]	Ring-opening[b] (%)	Fatty Acid[c] (%)
1[d]	1	100	25
2	1	100	20
3	0.8	100	0
4	1.2	100	25

[a] Concentration 1M, [b] Ring-opening determined by ^{1}H NMR. [C] fatty acid percentage determined by ^{1}H NMR and free fatty acid determination[165-166], [d] One-pot procedure.

Table 2.5: Ring opening optimisation of tungsten catalysed epoxidised cocoa butter.

While the use of 0.8 equivalents of 1M H_3PO_4 (entry 3) was initially encouraging the result could not repeated upon scale-up (>250 g scale) and hydrolysis was again observed. It was possible that either tungsten residues dissolved in the crude oil (and not fully removed by washing at the epoxide stage) or the levels of phase transfer catalyst carried over from the epoxide stage, were responsible for this undesired hydrolysis. In 2002, Petrovic *et al*. successfully epoxidised soybean oil with hydrogen peroxide, acetic acid and an ion exchange resin, Amberlite® IR-120 in toluene at 40, 60 and 80 °C.[93] Amberlite is an acidic polymer resin bead, which catalyses the oxidation of acetic acid to peroxyacetic acid, which subsequently reacts with the double bonds present in the oil without the need for either a tungsten or phase transfer catalyst.[167-170] This method was attempted on cocoa butter at 60 °C and afforded epoxidised cocoa butter in 88 % yield after 8 hours (Scheme 2.2). Acid value titrations again gave values of 10 and show only the presence of 4 % free fatty acid seen within the starting material. This was also confirmed with GPC analysis (Fig 2.9). Oxirane values, determined by titration with HBr, confirm full epoxidation of the double bonds with values of 1.62 % which relates to 1 mole of epoxide per mole of compound. This compares well with values obtained for the iodine value of the unsaturated starting material. Hydroxyl value titrations confirmed

the presence of hydroxyl groups with a value of 0 showing no hydroxyl groups present.

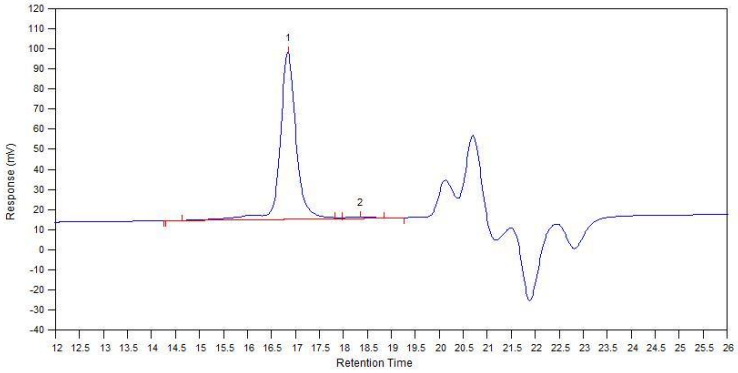
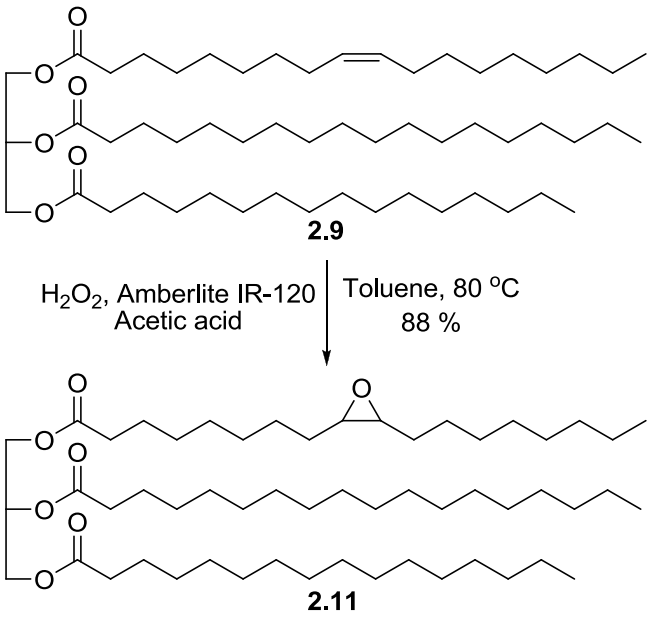


Figure 2.9: GPC trace of epoxidised cocoa butter diol.

With the epoxide **2.11** prepared by the Amberlite® protocol in hand (and free of tungsten or phase transfer catalyst residues) the ring-opening process was investigated with and without phase transfer catalyst at 100 °C on a 5 g scale. The amount of molar equivalents of H_3PO_4 was also varied (1 equiv. entries 1, 3 and 5, 0.25 equiv. entries 2 and 4) and its concentration (1M, entries 1, 2 and 5, 0.25 M entries 3 and 4), (Table 2.6).



Scheme 2.2: Epoxidation of cocoa butter using Amberlite® IR 120.

These results show (entry 1) that complete ring-opening without hydrolysis can be achieved with 1 equivalent of 1M H_3PO_4 at 100 °C for 24 hours. This reaction was reproducible on a 5 g, 100 g and 300 g scale (although for the 300 g scale the reaction required 26 hours). The result is suggestive of the fact that residual impurities from the tungsten catalysed epoxidation process may be responsible for the observed hydrolysis in the initial experiments.

Entry	H_3PO_4	Concentration (M)	Ring-opening[a] (%)	Fatty Acid[b] (%)
1[c]	1	1	100	0
2[c]	0.25	1	14	0
3[c]	1	0.25	11	0
4[c]	0.25	0.25	0	0
5[d]	1	1	0	0

[a] Ring-opening determined by ^{1}H NMR. [b] fatty acid percentage determined by ^{1}H NMR and free fatty acid determination.[165-166] [c] Phase transfer catalyst Adogen 464 0.25 wt% was added. [d] No phase transfer catalyst was added.

Table 2.6: Ring opening optimisation of 2.11 prepared using the Amberlite® method.

Acid value titrations gave values of 10 which show a presence of 4 % free fatty acid which compares with results obtained from the starting material, showing successful ring-opening without hydrolysis. This was also confirmed with GPC analysis where

only a small percentage of free fatty acid can be observed (Fig 2.10). Hydroxyl values confirm full ring opening of the epoxide with values of 77.

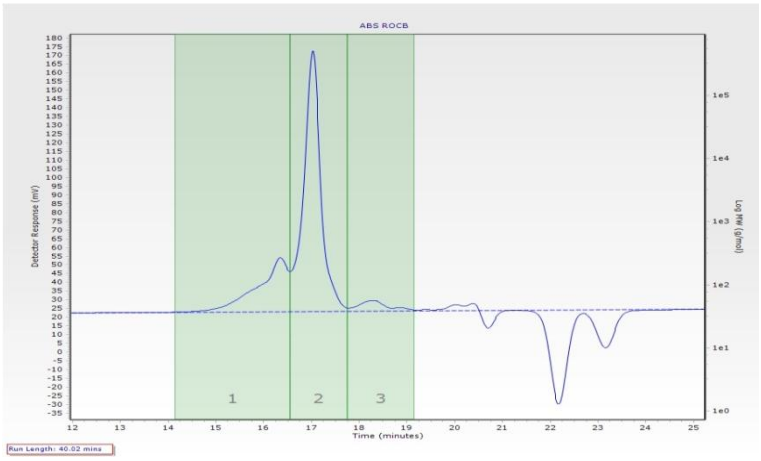


Figure 2.10: GPC trace of 2.10(0%).

Having achieved large scale ring-opening of epoxidised cocoa butter with both 0% hydrolysis **2.10(0%)** and 25% hydrolysis **2.10(25%)** samples were prepared to see what effect these two different polyol feedstocks had on the physical properties of the polyurethanes prepared from them. To complete the series, **2.10(100%)** was also prepared, where epoxidised cocoa butter **ECB 2.11** was ring-opened and then completely hydrolysed using sodium hydroxide in water at 100 °C overnight to give **2.10(100%)** in 92 % yield. Complete hydrolysis was confirmed with ^{1}H NMR showing complete removal of peaks characteristic of the glycerol backbone and acid values of 173 showing complete hydrolysis of the triglyceride. Hydroxyl value titrations confirmed the presence of hydroxyl groups with a value of 567. This is higher than **2.10(0%)** due to extra hydroxyl groups from the carboxylic acid groups present from hydrolysis.

Hydroxyl values were determined using a procedure outlined by Hartman *et al.*[171] Free fatty acid values were determined using the equation 2.1, (where Mw is an

average value determined by the statistical composition, Table 2.4, and N is the concentration of the KOH used in the acid value determination).

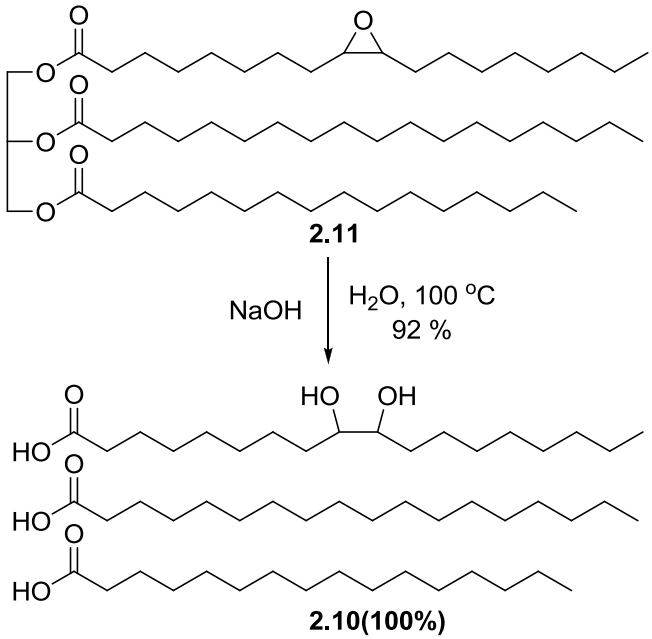
$$Free\ Fatty\ Acid = \frac{mL\ KOH\ x\ N\ x\ Mw\ (fatty\ acid)}{10\ x\ Wt\ sample\ used} \qquad Equation\ 2.1$$

Sample	OHV[a]	Acid Value[b]	Free Fatty Acid[b]
Epoxidised Cocoa Butter **(ECB 2.11)**	0	10	4%
2.10(0%) (renamed **2.10(4%)**	60	10	4%
2.10(25%)	77	59	29%
2.10(100%)	567	173	100%

[a] Hydroxyl value determined using hydroxyl value procedure.[171] [b] Acid value and free fatty acid determined using procedure produced by Lubrizol Corporation.[166]

Table 2.7: Hydroxyl, and acid values and free fatty acid % of cocoa butter samples CB 2.10.

Interestingly, the analysis indicated that epoxidised cocoa butter **ECB 2.11** contained 4 % of free fatty acids (too small to be detected by ^{1}H NMR). Consequently, in this thesis the name of polyol **2.10(0%)** has been changed to **2.10(4%)** to reflect the reality of percentage of free fatty acids measured in this monomer.



Scheme 2.3: Ring-opening and hydrolysis of epoxidised cocoa butter ECB 2.11.

2.3.2 Thermal analysis of cocoa butter based monomers 2.10

Before polymerisation was attempted of the monomers **2.10** thermal properties were investigated (Fig. 2.11) (Table 2.8).

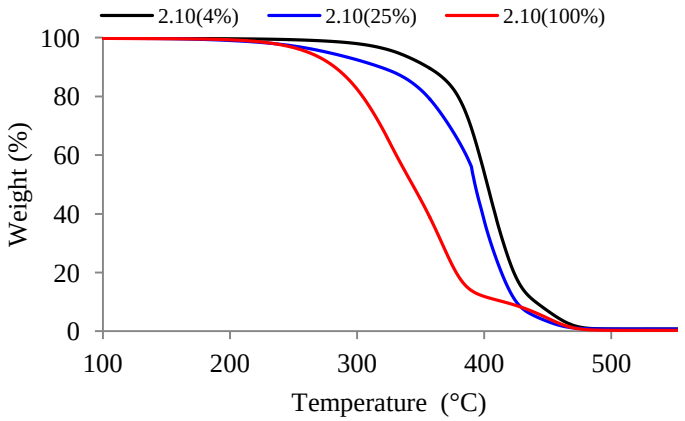


Figure 2.11: TGA of 2.10(4%), 2.10(25%) and 2.10(100%).

Monomer	DSC (°C)[a]	DSC (°C)[a]	TGA (°C)[a]		
	T_g	*Mpt*	T_{10}	T_{50}	T_{max}
2.10(4%)	-[b]	23, 55	357	403	507
2.10(25%)	-42	44	321	393	507
2.10(100%)	-42	53	284	344	484

[a] DSC and TGA values measured using 10 °C /min. [b] No glass transition was detected for **2.10(0%)** between -100 to 100 °C.

Table 2.8: Thermal analysis of 2.10(4%), 2.10(25%) and 2.10(100%).

Cocoa butter displays polymorphism, having α, γ, β', and β crystalline forms, with melting points measured as 23 °C, 17 °C, 26-28 °C, and 35–37 °C respectively.[172] Monomer **2.10(4%)** shows two melting points at 23 °C and 55 °C suggestive of a phase change from one polymorph to another. The main melting points for all three monomers are in the range 44-53 °C somewhat higher than cocoa butter. The glass transition temperature (T_g) of **2.10(25%)** and **2.10(100%)** are similar irrespective of the free fatty acid percentage and this observation agrees with the results reported by

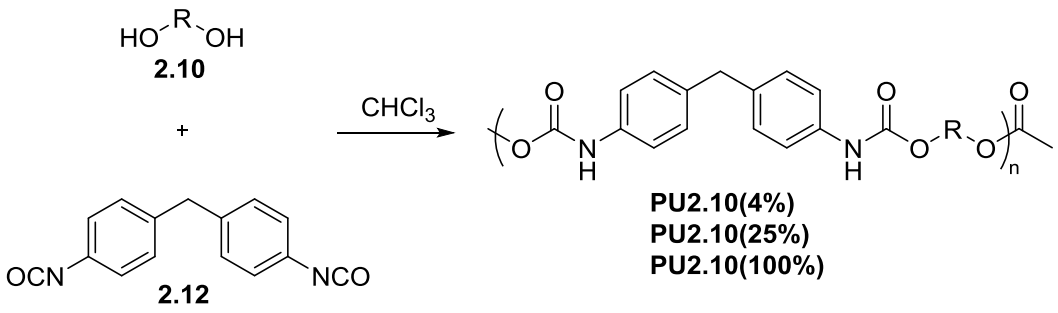
Cedeño *et al*. during their thermal studies of free, binary and ternary mixtures of fatty acids.[173] The thermal stability of the monomers varies significantly and is characteristic of the percentage of free fatty acid present in the monomer which parallels similar trends to those seen in castor oil by Goodrum *et al*. during their thermal studies of medium and long-chained triglycerides.[174] Triglycerides generally have a higher thermal stability than their corresponding acids. In fact, the level of free fatty acids within a triglyceride mixture can be determined by their thermal degradation profile.[175] The values for **2.10(100%)** compare well with those seen by Borugadda *et al*. when studying castor oil derived methyl esters.[176]

2.4 Cocoa butter based polyurethanes.

2.4.1 Polyurethane synthesis of PU 2.10(4%), PU 2.10(25%) and PU 2.10(100%),

The majority of published work on the synthesis and properties of polyurethanes (PU's) derived from renewable vegetable oils has focussed upon MDI based materials.[117-118,177-179] Consequently polymerisation between monomers **2.10(4%)**, **2.10(25%)** and **2.10(100%)** and MDI **2.12** were investigated, (Scheme 2.4). A ratio of 1.05:1.00 (isocyanate:OH group) was used to ensure all hydroxyl groups in the cocoa butter monomers **2.10** polymerised and any excess isocyanate **2.12** reacted with the moisture in the air during the curing process. Polymerisations were attempted with or without solvent ($CHCl_3$). Initially, both the monomer **2.10** and diisocyanate **2.12** was dissolved in $CHCl_3$ at room temperature and cast into a mould. However, this caused bubbles to form in the polymer during the curing process, (presumably due to released H_2O from residual water contained within the

monomers **2.10**), and as a result the samples were not suitable for mechanical testing, (Scheme 2.4). Attempts to carry out the polymerisations in a vacuum oven (at 60 °C, -760 mmHg), caused even larger bubbles due to curing continuing whilst the solvent and air was being removed.



Scheme 2.4: Polyurethane synthesis PU2.10 using solvent.

An alternative solvent-free approach was more successful. In this approach, the cocoa butter monomer **2.10** was heated to 60 °C under vacuum for 1 hour to remove air and residual solvent, MDI was added and the vacuum reapplied for 2 mins at 60 °C during which time the mixture was stirred gently to prevent air becoming trapped in the polymer (Scheme 2.5). The monomer was then cast into a mould (Fig. 2.12) and cured at 60 °C overnight. This produced samples **2.10(4%)** and **2.10(25%)** with no bubbles which were suitable for mechanical testing.

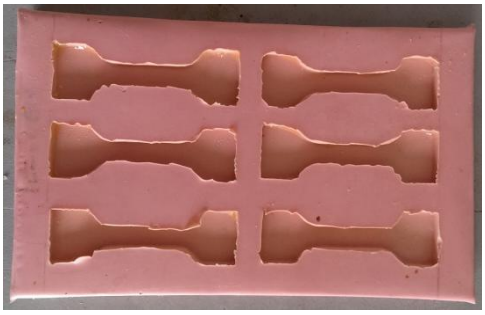
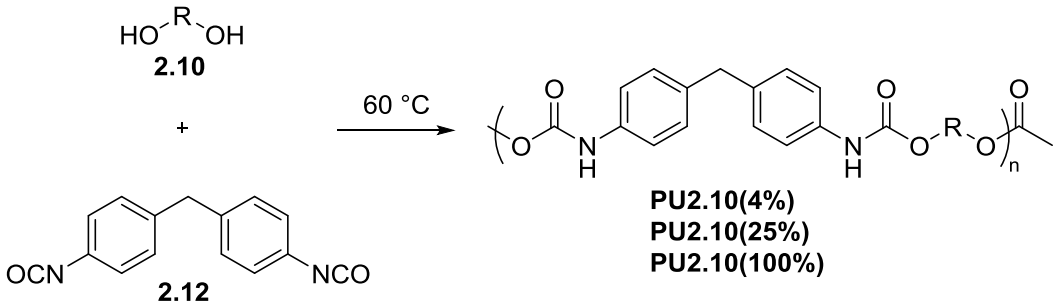
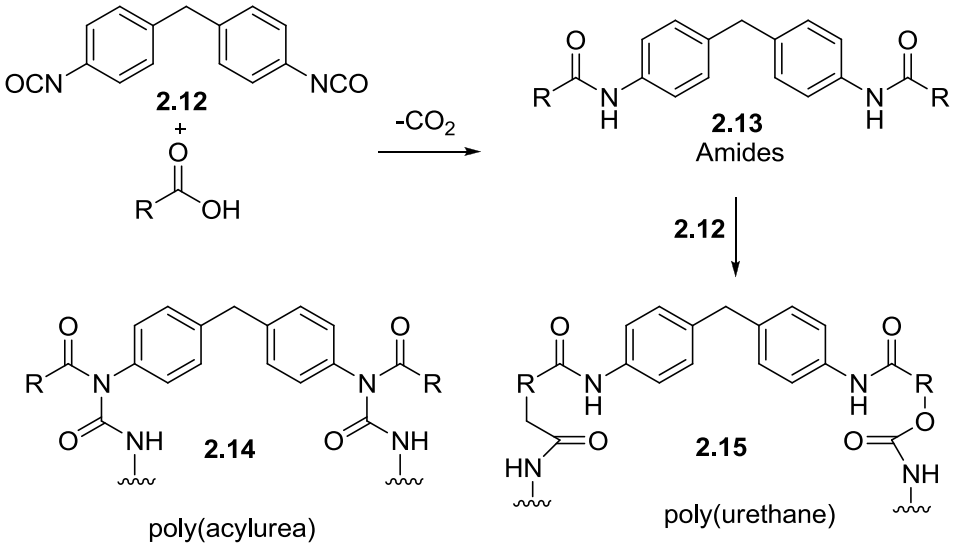


Figure 2.12: Silicone mould used for casting dog-bones.



Scheme 2.5: Solvent-free polyurethane PU2.10 synthesis.

Reaction of **2.10(4%)** with MDI **2.12** would be expected to produce the polyurethane **PU2.10(4%),** however, the outcome of the reaction of **2.10(25%)** and **2.10(100%)** is less certain. These monomers also contain mixtures of saturated carboxylic acids (palmitic **1.20**, stearic **1.21**), hydroxylated carboxylic acids (9,10-dihydroxystearic acid derivative of oleic acid **1.22**), and mono-and digylcerides of the above fatty acids. For example, saturated carboxylic acids are known to react with isocyanates to form carbamic-carboxylic anhydrides which are unstable and decompose to form amides **2.13** and CO_2, (Scheme 2.6).[180] These amides **2.13** can go onto react with MDI to give poly(acylureas) **2.14**. Alternatively, if an R group contains dihydroxy functionality **2.13** then these can react further with MDI **2.12** to form amide cross-linked polyurethanes **2.15**. In addition **2.10(25%)** contains significant amounts of diglyceride monomers containing on average 3 hydroxy groups. These monomers will be able to crosslink during the polymerisation process. GPC data was not obtainable as Pus synthesised were not soluble in organic solvents or water. This is presumably due to the degree of cross linking or hydrophobicity of the aliphatic polyol.



Scheme 2.6: Possible products from reaction of 2.10(25%) and 2.10(100%) with MDI 2.12.

2.4.2 Thermal analysis of cocoa butter based polyurethanes

DSC of the polyurethanes can be seen in appendix 1, tabulated results are below (Table 2.10). Polymerisation, as expected, has increased the T_g (***2.10(25%)*** T_g *= -42 °C,* ***PU2.10(25%)*** T_g *= -7 °C,* ΔT_g *= 35 °C*). Carboxylic acids can react with isocyanate groups to form carbamic-carboxylic anhydrides which are unstable and decompose to form amides which may react further to give ureas.[180] The amount of this side-reaction will be determined by the percentage of fatty acids present in the monomer. Increasing the fatty acids percentage has increased the T_g values, **PU*2.10(4%)*** → **PU*2.10(25%)*** ΔT_g = 8 °C → **PU*2.10(100%)*** ΔT_g = 39 °C. However, the T_g for the cocoa butter based polyurethane **PU*2.10(4%)*** is lower than those synthesised by Petrovic *et al*. with other triglycerides due to the lack of cross-linking caused by the low hydroxyl number. This follows the trend seen where lower hydroxyl values give lower glass transition temperatures.[156] Cocoa butter **2.10(4%)** only has 2 hydroxyl groups when fully ring-opened whereas the vegetable oils used by Petrovic *et al*.[95] have more hydroxyl groups (e.g midoleic sunflower oil

has 4 hydroxyl groups): T_g (***PU2.10(4%)*** T_g *= -15 °C, midoleic sunflower oil* T_g *= 24 °C* ΔT_g *= 39 °C*).[156]

Monomer	DSC (°C)[a]	TGA (°C)[a]			Sol Fraction %[b]
	T_g	T_{10}	T_{50}	T_{max}	
2.10(4%)	-[b]	357	403	507	-
2.10(25%)	-42	321	393	507	-
2.10(100%)	-42	284	344	484	-
PU2.10(4%)	-15	353	435	518	13
PU2.10(25%)	-7	312	393	512	39
PU2.10(100%)	32	344	421	509	-

[a] DSC and TGA values measured using 10 °C /min. [b] No glass transition was observed for **2.5b** between -100 to 600 °C, [b]Sol fraction determined using THF and Soxhlet apparatus

Table 2.9: Thermal analysis of 2.10 monomers and PU2.10 polyurethanes.

Thermal stability of the **PU** polymers containing lower fatty acid content **PU2.10(4%)** and **PU2.10(25%)** has decreased slightly while that derived from 100% fatty acids **PU2.10(100%)** has increased (this polymer is almost certainly not a PU). Both **PU2.10(4%)** and **PU2.10(25%)** show a two-step degradation which is correspondent of vegetable oil based polyurethanes with a small initial weight loss (< 5 %) caused by the degradation of the urethane link in which carbon dioxide is lost.[116] This is not so visible in **PU2.10(100%)** and is likely due to the presence of amide and urea bonds. **PU2.10(100%)** has a higher residue at T_{max} as a consequence, (Fig. 2.13).

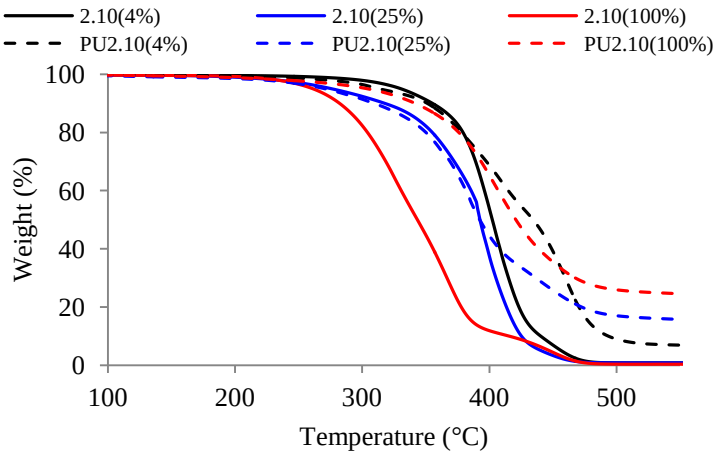


Figure 2.13: TGA comparison of 2.10 monomers and PU2.10 polyurethanes.

2.4.3 Mechanical testing of PU2.10(4%) and PU2.10(25%)

The polymer **PU2.10(100%)** was not subjected to tensile mechanical testing due to the samples being too brittle and full of bubbles caused by the loss of CO_2 during the decomposition to form the amide bond previously mentioned. The brittleness is caused by the short chained nature of the polymers. Ring-opened epoxidised oleic acid formed short chained polyurethanes through the diol and an amide through the carboxylic acid however the saturated fatty acids will form dimers with MDI or terminate the ring-opened oleic acid polyurethane. Both other samples, **PU2.10(4%)** and **PU2.10(25%)** were subjected to mechanical testing (Table 2.10).

Polymer	UTS (MPa)	EoB (%)	YM (MPa)
PU2.10(4%)	3.2 (±0.6)	83 (±24)	2.7 (±0.3)
PU2.10(25%)	4.5 (± 0.9)	268 (±52)	1.2 (±0.1)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 2.10: Mechanical testing of PU2.10(4%) and PU2.10(25%).

Polymer **PU2.10(25%)** has a higher tensile strength compared with **PU2.10(4%)** This is likely to be due to the significant amount of diglyceride, (containing 3 OH groups) in the renewable monomer, and due to the extra hydrogen bonding possibilities caused by any amide or urea linkages caused by reaction of MDI with carboxylic acids, (Fig. 2.14). Polymer **PU2.10(4%)** has a lower tensile strength compared to those materials synthesised by Petrovic *et al*. (***PU2.10(4%)*** *UTS = 3.2 MPa, midoleic sunflower oil UTS = 14.8 MPa, ΔUTS = -11.6 MPa*) and this is due to the lower hydroxyl values of the original monomers and consequently, less cross-linking. Both samples show a small amount of necking around 25 % strain where the samples then begin to strain harden briefly before showing yield points around 50 % strain where the polymer has past its elastic limit and is now deforming plastically.

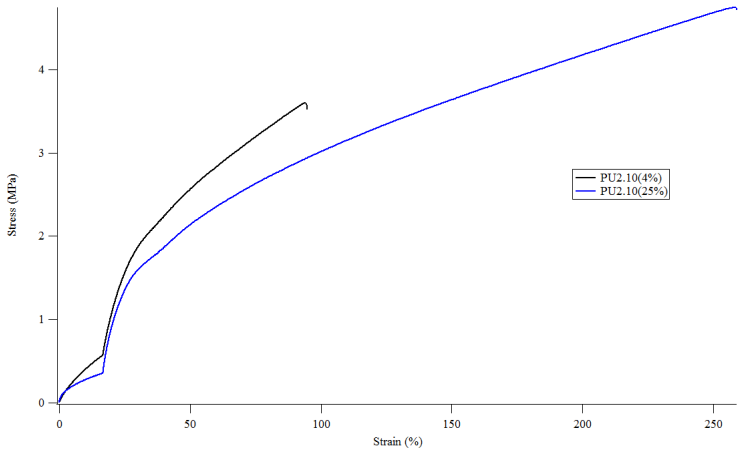


Figure 2.14: Stress strain curves of PU2.10(4%) and PU2.10(25%).

2.5 Dyed cocoa butter based polyurethanes

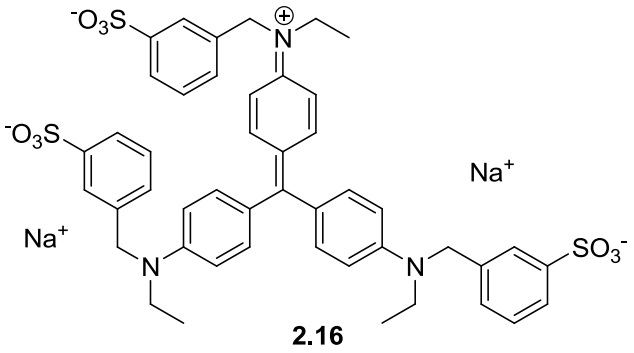
2.5.1 Addition of dye to cocoa butter based polyurethanes

Polyurethanes come in various colours and colour is added in two ways, either to the monomer prior to polymerisation or during polymerisation.[181] The structure of the added dyes either has to include a diol, to become incorporated into the polymer network, or other functional groups capable of covalently bonding to the isocyanate.[182] Alternatively, dyes can be absorbed onto polymers and may interact via H-bonding or electrostatic interactions.[183]

Dyes can be added as dispersions in the diol monomers however, these could lead to dye leaching from the polyurethane. In 2013, Ramazanova *et al*. successfully dyed polyurethane foams with food dyes post polymerisation using aqueous solutions of the dyes at a range of pH's, the sorption of dyes in polyurethanes is believed to occur due to electrostatic interactions of anionic particles with basic groups in the polyurethane network.[184]

As food dyes can be incorporated into polyurethanes post curing and as cocoa butter is a waste food product samples were prepared to test if food dyes could be incorporated into the polyurethane network prior to the polymerisation process and what effect this had on the thermal and physical properties. The addition of water soluble food dyes into the hydrophobic vegetable derived materials might be problematic and phase separation might be observed.

Brilliant blue FCF **2.16** (Fig. 2.15) was initially chosen due to the lack of hydroxyl groups present in the structure which would not directly react with the MDI and form a covalent link with the polymer. Although sulfonic acid groups are known to react with isocyanates the reactions can be reversible.[185-186] The polyurethane was synthesised using the same procedure used in section 2.4 with 10 mg of dye added to the cocoa butter monomer prior to the MDI.



2.16

Figure 2.15: Structure of Brilliant blue FCF 2.16.

2.5.2 Thermal analysis of 2.16PU2.10(4%) and 2.16PU2.10(25%)

DSC shows little change in T_g between polymers with and without dye incorporated, (Table 2.12, Fig. 2.16). Similar observations were made by Wang and Gen when comparing waterborne polyurethanes with covalently attached dyes.[187] Both dyed polymers have similar decomposition profiles. Initial thermal stability (T_{10}) has decreased by 8 °C for **2.16PU2.10(25%)** and 13 °C for **2.16PU2.10(4%)** caused by the thermal decomposition of brilliant blue FCF **2.16** which can be seen by the initial degradation at around 280 °C (Fig. 2.17) which corresponds to the melting/decomposition point of brilliant blue FCF.[188]

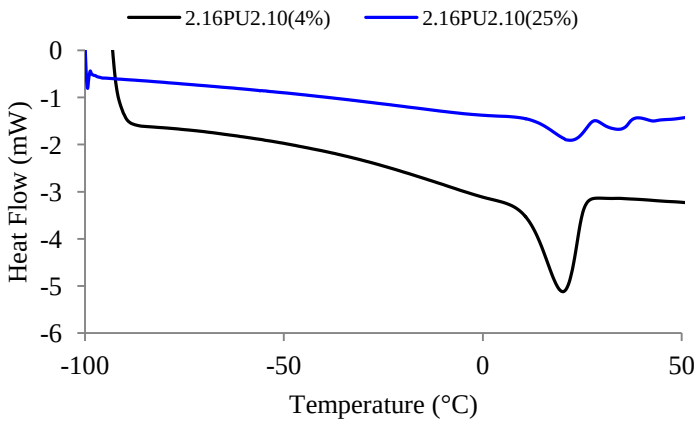


Figure 2.16: DSC of 2.16PU2.10(4%) and 2.16PU2.10(25%) polymers.

Polymer	DSC (°C)[a]	TGA (°C)[a]			Sol Fraction (%)[b]
	T_g	T_{10}	T_{50}	T_{max}	
PU2.10(4%)	-15	353	435	518	13
PU2.10(25%)	-7	312	393	512	39
2.16PU2.10(4%)	-21	340	429	523	64
2.16PU2.10(25%)	-6	304	429	531	38

[a] DSC and TGA values measured using 10 °C /min. [b]Sol fraction determined using THF and Soxhlet apparatus

Table 2.11: Thermal comparison of dyed 2.16PU2.10 and non-dyed PU2.10 polymers.

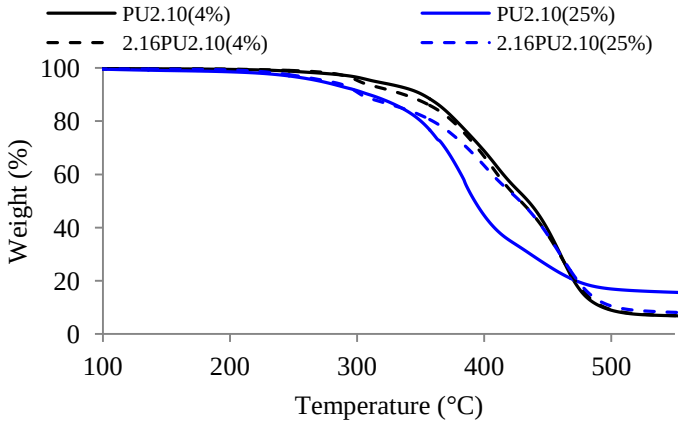


Figure 2.17: TGA comparison of dyed 2.16 PU2.10 and non-dyed PU2.10 polymers.

While the thermal profile for **2.16PU2.10(4%)** and **PU2.10(4%)** are similar, there is a significant difference between **2.16PU2.10(25%)** and **PU2.10(25%)**. The main difference between the **PU2.10(4%)** and **PU2.10(25%)** class is the level of cross-linking, amide and urea linkages and possibly pH (residue fatty acids within polymer matrix). Both T_{50} and T_{max} of **2.16PU2.10(25%)** has increased with the addition of the dye, this could be caused by the increase in hydrogen bonding between the amide/urea bonds and the sulfonate groups on the dye.[189]

2.5.3 Discolouration of PU2.10 and leaching of dye form 2.16PU2.10 over time

The level of fatty acid present in the monomer **2.10** was shown to have an effect on the colour of the polyurethane **PU2.10** over time (Table 2.13). Unsaturated fatty acids have been known to undergo autoxidation to form a ketone in the position of one of the double bonds which causes yellowing of the sample over time.[190] In addition, aromatic polyurethanes also undergo oxidative yellowing over time upon exposure to UV radiation, this process is known to be accelerated by acid, and high humidity and involves oxidation of aromatic amines to quinones.[191-192] These amines might be present due to hydrolysis of the urethane linkages or by reaction of the isocyanate with carboxylic acids as well as the diurethane bridge.[193] Dyes, UV absorbers or antioxidants are often incorporated to retard or disguise discolouration over time. Discoloration is often increased by amino groups or metal impurities.[194] Consequently, we would predict that discolouration of **PU2.10(25%)** should be faster than **PU2.10(4%)**. Over a 1 year time frame we observe this to be the case, (Table 2.13). Incorporation of the dye **2.16** does not retard the discolouration; instead the blue colour slowly changes to green over the same time frame,

Polymer	Initial Colour	Colour over time
PU2.10(4%)	Cream	Cream
PU2.10(25%)	Cream	Amber
2.16PU2.10(4%)	Blue	Blue
2.16PU2.10(25%)	Blue	Green

Samples left in storage in dark conditions for 1 year

Table 2.12: Colour of cocoa butter based polyurethanes.

Tests were carried out into the leaching of the dye **2.16** from the **2.16PU2.10(4%)** and **2.16PU2.10(25%)**. Both dyed polyurethane samples were submerged in water for 1 day, 2 days and 7 days to determine the percentage of incorporated dye **2.16**

that leached out. Samples were analysed by UV and concentrations determined using a calibration curve (Fig. 2.18, Table 2.14).

Sample	1 day (%)	2 days (%)	7 days (%)
2.16PU2.10(4%)	0.1	0.2	0.5
2.16PU2.10(25%)	0.2	0.1	0.1

Percentage of dye added dye leached from polyurethane samples

Table 2.13: Dye 2.16 leached from polyurethanes 2.16PU2.10(4%) and 2.16PU2.10(4%).

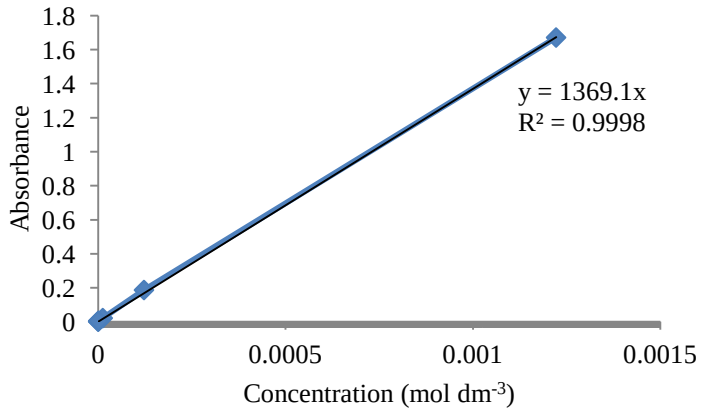


Figure 2.18: Brilliant blue 2.16 absorbance-concentration calibration curve.

The results show that even after 7 days the amount of dye **2.16** leached from the sample is very low, suggestive that the dye **2.16** is strongly bound within the polymer network. Binding might be covalent through reaction of the dye sulfonate groups with the isocyanate functionality, however Ballé *et al*. has reported cleavage of this type of bond *via* reaction with water. It should be highlighted that it is unlikely that water would be able to penetrate into the polymer network due to the hydrophobicity of the polyurethane caused by the presence of the triglyceride functionality.[189]

2.5.4 Mechanical testing of 2.16PU2.10(4%) and 2.16PU2.10(25%)

Incorporation of the dye **2.16** was found to have decreased the tensile strength of both **PU2.10(4%)** and **PU2.10(25%)** by 2.9 MPa and 3.3 MPa respectively, (Table 2.13), stress strain curves can be found in appendix 1.

Polymer	UTS (MPa)[a]	EoB (%)[a]	YM (MPa)[a]
PU2.10(4%)	3.2 (±0.6)	83 (±24)	2.7 (±0.3)
PU2.10(25%)	4.5 (± 0.9)	268 (±52)	1.2 (±0.1)
2.16PU2.10(4%)	0.3 (±0.1)	163 (±52)	0.26 (±0.1)
2.16PU2.10(25%)	1.2 (±0.1)	116 (±8)	1.49 (±0.2)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 2.14: Mechanical testing comparison of dyed 2.16PU2.10 and non-dyed PU2.10 polyurethanes.

For **2.16PU2.10(4%)** the elongation at break has doubled due to the increased hydrogen bonding ability as a result of the sulfonate groups and the urethane links. Elongation for **2.16PU2.10(25%)** has decreased and is potentially due to the free hydroxyl group present in the mono- and di-glyceride reacting with the sulfonate groups present in the brilliant blue dye, similar to the method employed by Wang *et al*. to graft dyes onto modified waterborne polyurethanes, decreasing the amount of available cross-linking.[187]

2.6 Summary and conclusion

Waste cocoa butter triglyceride **2.9** can be epoxidised **2.11** and successfully ring opened to give **2.10**, either in 1 step (without isolating the epoxide) or 2 steps. The one step process leads to 25 % hydrolysis of the triglyceride, forming a diglyceride

and free fatty acids. The two step protocol allows isolation of the epoxide **2.11** prior to ring-opening. Epoxidation using Amberlite IR-120, acetic acid and hydrogen peroxide in toluene was more successful than the use of W and a phase transfer catalyst. Ring-opening was achieved without ester hydrolysis on a small scale, 5 g reaction, using 1 equivalent of 1 M acid with respect to the **2.11** at 100 °C in 24 hours. Results were reproducible on 5 g scale and could be successfully scaled up to 100 g and 300 g, however sufficient heat transfer is required on the larger scale as the 300 g reaction took 26 hours for full ring-opening.

Polyurethanes were synthesised from diol monomers **2.10** containing varying levels of fatty acids **2.10(4%)**, **2.10(25%)** and **2.10(100%)**. The polymers **PU2.10** exhibited an increase in T_g, dependent upon the fatty acid % of the initial monomer (**PU2.10(4%)** T_g = -15 ºC, **PU2.10(25%)** T_g = -7 ºC and **PU2.10(100%)** T_g = 32 ºC. This is thought to be due the relative increase in amide and urea bond formation caused by reaction of the free fatty acids in the monomers **2.10** with the MDI isocyanate groups and for **PU2.10(25%)** the possibility of cross-linking due to the presence of triols. Degradation of **PU2.10(4%)** and **PU2.10(25%)** shows the characteristic initial degradation of the urethane linkages as expected, while the material from **PU2.10(100%)** has the greatest thermal stability due to the formation of significant amounts of amide or urea bonds. Mechanical testing of **PU2.10(4%)** and **PU2.10(25%)** also showed increased tensile strength for the material containing greater amide / urea linkages.

Addition of a food safe dye **2.16** to the polyurethane caused a decrease in thermal stability and tensile strength. The lower thermal stability is thought to be due the decomposition of brilliant blue FCF dye or the cleavage of carbamic-sulfonate anhydrides formed on reaction of the sulfonic acids in **2.16** with MDI. The T_{50} of

2.16PU2.10(25%) was greater than for **PU2.10(25%)**. A possible explanation for this is the increase in hydrogen bonding upon addition of the dye **2.16** with the increased amide / urea bonds compared to **PU2.10(4%)**.

All polyurethanes exhibited colour changes over time (1 year) due to the aromatic nature of the diisocyanate and this could not be disguised by incorporating a dye **2.16**.

Since this work was undertaken there has been a global shortage of cocoa beans due to black pod disease and bug infestations, therefore there is a shortage of cocoa butter and cocoa powder. Should the production start to increase in the future, and costs decline, then cocoa butter would prove to be an ideal renewable monomer for further study.

2.7 Future Work

While the dye brilliant blue **2.16**, containing sulfonate groups, can be incorporated into renewable polyurethanes from cocoa butter, it causes a lowering of the tensile strength of material. This may be due to the formation of weak and reactive carbamic-sulfonate anhydrides. Further research into how other dyes (such as **2.17-2.19,** Fig 2.19), containing hydroxyl groups capable of incorporation as urethane linkages, affect the tensile strength and elongation of the polyurethanes could be undertaken in order to prepare materials with greater strengths and stabilities.

Addition of hard segments, such as butanediol and PEG, could be studied and the physical and thermal properties analysed and compared with those currently available for other renewable triglycerides such as commercial palm oil and soybean

oil to see how a waste triglyceride feedstock from the confectionary industry compares and with the use of the environmentally unfriendly alternatives.

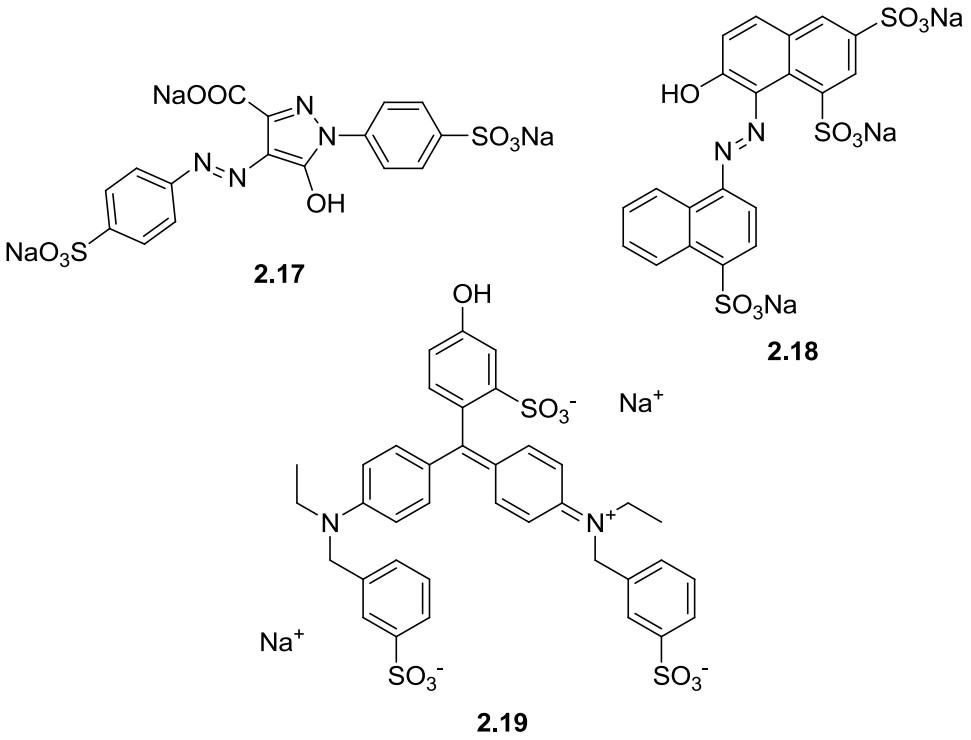


Figure 2.19: Alternative food safe dyes containing hydroxyl groups.

The Clark group has carried out a large amount of research on the $BF_3.OEt_2$ mediated co-ring-opening of vegetable oil epoxides and THF to give p(THF) grafted vegetable oil polyols. Blending cocoa butter diol into these monomers will allow tailoring of the OH number and physical properties of the materials, to match more closely commercially available polyurethanes in a bid to increase the percentage of renewable materials industrially available.

3.0 Synthesis of Alkyne-Azide Click Polymers Derived from Renewable Oils

3.1 Introduction

The synthesis of azide-alkyne click polymers derived from renewable oils is a relatively new area of research.[138-139] In 2010, Shah *et al.* first investigated the azide-alkyne Huisgen cycloadditions of suitably functionalised soybean oil derivatives.[138] The oil was functionalised in two ways to give two distinct monomers **3.1** and **3.2**, (Fig. 3.1). The first monomer synthesised was alkynated soybean oil **3.1**, this was subsequently reacted with aliphatic **3.3** and aromatic **3.4** diazides to give the cross-linked polymers **3.7** and **3.8**, (Fig. 3.2).

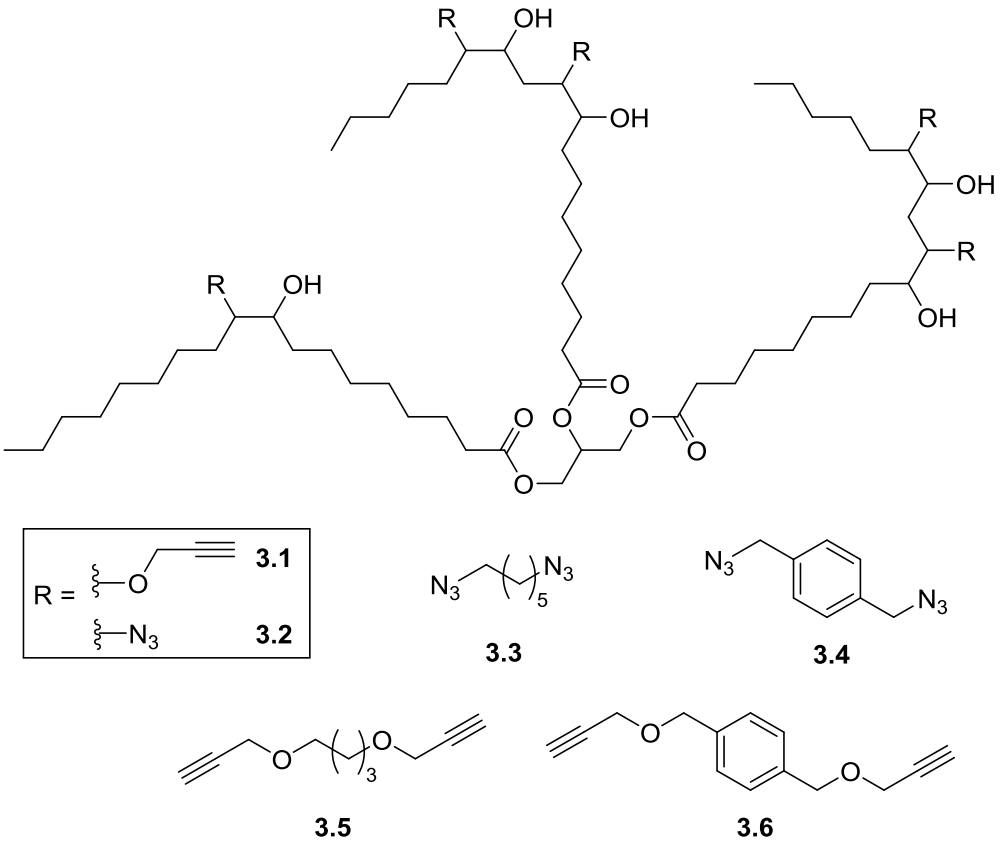


Figure 3.1: Functionalised soybean oil and diazide and dialkyne compounds.

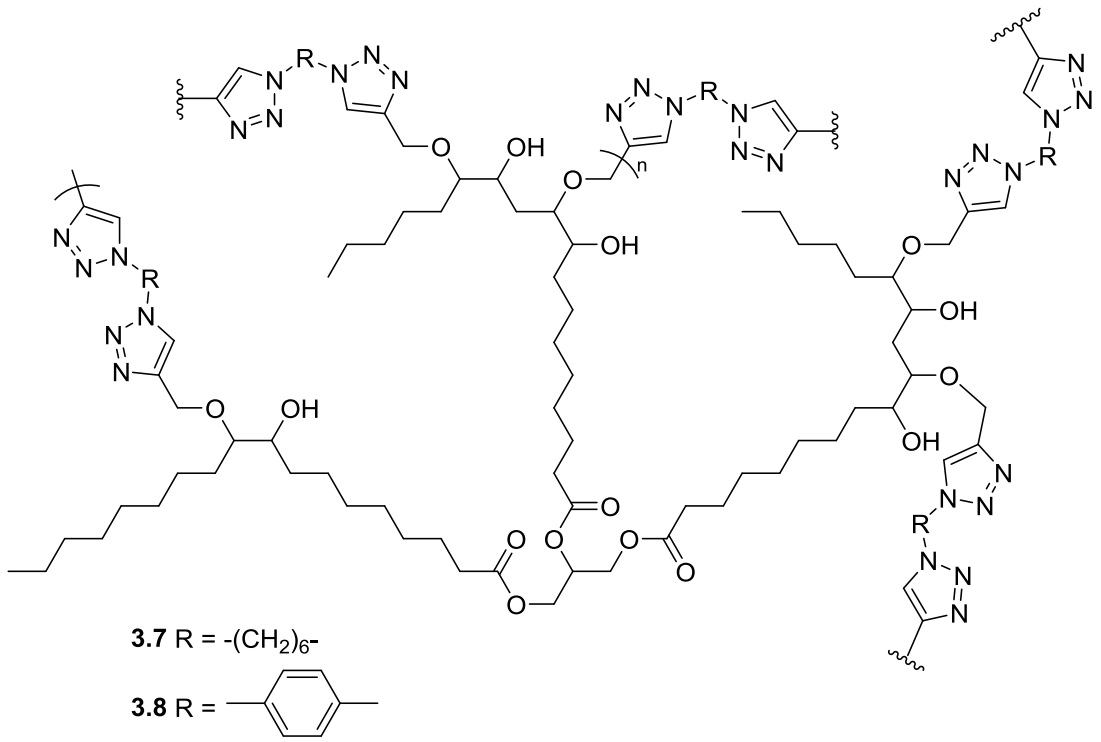


Figure 3.2: Polymers derived from alkynated soybean oil 3.1.

Alternatively, epoxidised soybean oil **2.1** was ring opened with sodium azide to afford the azido soybean oil **3.2** in ~95 % yield. This monomer was reacted with dialkyne derivatives **3.5** and **3.6** to give a similar range of polymers **3.9** and **3.10**, (Fig. 3.3).

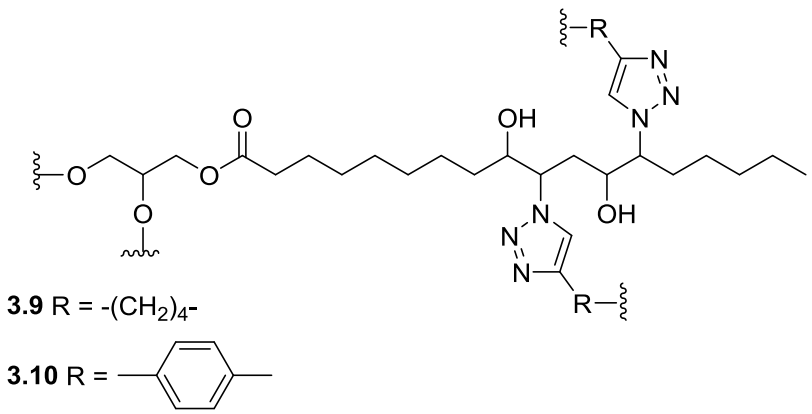


Figure 3.3: Polymers derived from azidanated soybean oil 3.2.

The group carried out the polymerisations in two ways, using either copper catalysis or by a thermal reaction alone. The initial approach however was *via* a copper (I) catalysed route using $CuSO_4$ and sodium ascorbate in DMF: water (10:1) at room temperature in 48 – 72 hours (Scheme 3.1). This provided materials with yields of between 65 – 85%. Thermal analysis data can be seen in table 3.1.

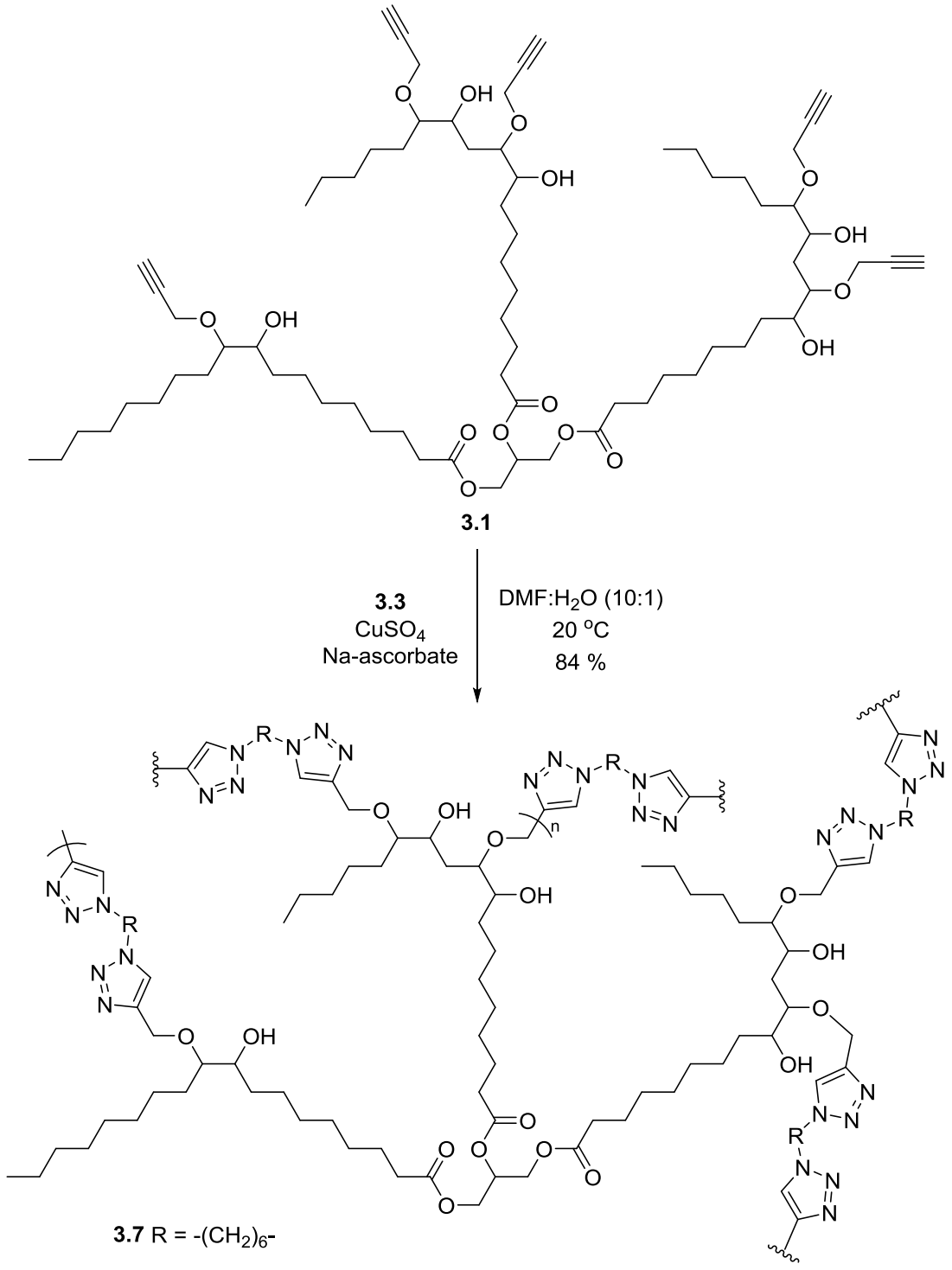
Polymer	Monomer 1	Monomer 2	T_g[a] (°C)	T_{10}[a] (°C)	T_{50}[a] (°C)
3.7	**3.1** (alkyne)	**3.3** (azide)	9 (-13)	335 (363)	401 (408)
3.8	**3.1** (alkyne)	**3.4** (azide)	10 (2)	316 (361)	395 (404)
3.9	**3.2** (azide)	**3.5** (alkyne)	80 (45)	313 (331)	397 (398)
3.10	**3.2** (azide)	**3.6** (alkyne)	-[b] (97)	322 (333)	399 (403)

[a] T_g, T_{10} and T_{50} values for $CuSO_4$ method, values in brackets are for thermal method. DSC and TGA values measured using 10 °C /min. [b] No glass transition was observed for **3.10** between -80 to 160 °C.

Table 3.1: Thermal properties of polymers prepared using Cu catalysis or heat.

The alternative thermal reaction was achieved by heating the functionalised oils **3.1** or **3.2** with the appropriate linker **3.3-3.6** at 100 °C for 12-24 hours. This provided polymers with higher yields (80 – 97 %), compared to the copper approach (65 – 85 %). Thermal analysis (Table 3.1) shows the copper catalysed process gave materials that generally had higher glass transition temperatures (T_g) and T_{10} values than those synthesised *via* the thermal method (e.g polymer **3.7**: T_g *copper = 9 °C* > T_g *thermal = -13 °C).* This was rationalised to be due to the residual $CuSO_4$ trapped within the polymer network, and further evidence for this was provided by the difference in colour of the polymers derived using the copper route. These polymers were green in colour compared with a yellowy colour for the thermally derived polymers. Thermal degradation was also affected by copper residues with those prepared by this route having a broader degradation range than those prepared *via* the thermal process. The polymers produced with the azidated soybean oil **3.2** generally showed

higher T_g's than those derived from **3.1**, irrespective of whichever approach to their synthesis was undertaken.



Scheme 3.1: Alkylated and azidated soybean copper catalysed click reaction.

Polymers were also synthesised by reacting both the alkynated **3.1** and azidated **3.2** oils directly providing renewable polymer **3.11**, where both monomers were derived from renewable sources. In 2012 Shah *et al.* expanded this chemistry further by synthesising a range of azidated oils derived from different vegetable oils *via* their epoxides.[139] The group used a range of oils with varying amounts of unsaturation, ultimately leading to a varied amount of azide functionality (Fig. 3.4).

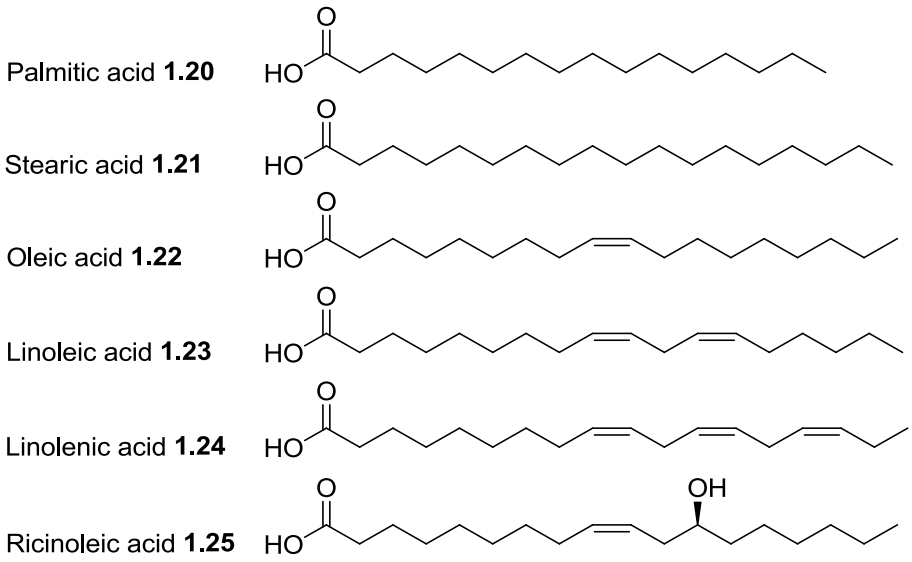


Figure 3.4: Common fatty acids in plant oils.

Castor **3.12**, canola (rapeseed) **3.13**, corn **3.14**, soybean **3.2**, and linseed **3.15** oils were azidated using the methods previously employed. The azide content was determined by elemental analysis and ranged from 3.2 azide groups per monomer in castor oil **3.12** up to 6.2 in linseed oil **3.15**. These monomers were polymerised thermally to produce samples suitable for mechanical testing. Thermal testing of the polymers (derived from: castor **3.16**, canola **3.17**, corn **3.18**, soybean **3.11** and linseed **3.19**) showed that the higher the azide functionality the higher the T_g, tensile strength and elongation at break of the polymer produced from it, although the

opposite was seen with the degree of swelling (Table 3.2). The material produced from castor oil **3.16** didn't follow this trend with both the T_g and elongation at break higher than predicted based upon its azide value. This was rationalised to be due to the extra hydroxyl group present in the ricinoleic derived side-chains (**1.25**) causing extra H-bonding interactions between chains. They concluded that in general an increase in the unsaturation of the starting oil allows an increase in azide functionality of the monomer which in turn causes an increase in mechanical and thermal properties of the polymer due to cross-linking.

Polymer	Monomer 1 (alkyne)	Monomer 2 (azide)	N_f[a]	T_g[b] (°C)	TS[c] (MPa)	Elongation at break[d] (%)
3.11	**3.1**	**3.2** (soybean)	4.6	10	1.3	40 (72)
3.16	**3.1**	**3.12** (castor)	2.9	1	0.6	54 (72)
3.17	**3.1**	**3.13** (canola)	4.2	-5	0.9	31 (81)
3.18	**3.1**	**3.14** (corn)	4.5	1	1.1	40 (76)
3.19	**3.1**	**3.15** (linseed)	6.2	16	3.4	61 (57)

[a] Number of the azide groups (Nf) per triglyceride was calculated using the equation: Nf = (Mn × nitrogen content)/(molecular mass of the azide group×100). [b] Scan rate for DSC measured using 10 °C /min. [c] TS = Tensile strength. [d] Values in brackets are for degree of swelling.

Table 3.2: Thermal and physical properties of Shah *et al*. biopolymers.

More recently in 2013, Bakhshi *et al*. synthesised soybean oil derived 1,2,3-triazole polyurethanes which showed a range of antibacterial activity towards *E. coli, S. aureus* and *C. albicans*.[195]

In summary:

- Various azide-click polymers (**3.11**, **3.16** – **3.19**) could be produced from a range of vegetable oils with varying levels of unsaturation.
- Polymerisation was successful using heat (100 °C) or copper catalysis (Cu(AAC)) but gave short network chains.

- Thermal onset of degradation was approximately 300 °C but a wider range of degradation temperatures were found for materials prepared *via* copper catalysis.
- Tensile strengths were relatively low (0.6 – 3.4 MPa) with elongations at break ranging from 30-60%.
- T_g's were found to range from -13 °C to 80 °C with those materials derived using copper catalysis generally showing higher values.
- Results indicated that by increasing H-bonding in chains (castor oil) elongation at break may be improved without the need for greater azide functionality.
- Materials made from 1,2,3-triazole derived vegetable oils show antibacterial properties.

3.2 Aims and objectives

The materials produced by Shah *et al*. **3.7-3.19** had relatively low tensile strengths (0.6 – 3.4 MPa) and elasticity's. Inspired by the increased elongation at break of the castor oil derivatives **3.12**, hinting that H-bonding between chains was important, and as part of the Clark group's interest in renewable elastomers *investigations were carried out to establish whether azide-click chemistry could be used to prepare more elastic materials without a decrease in tensile strength.* To this end:

- A range of dimeric fatty amides (capable of H-bonding) containing azide functional groups were prepared where the nature of the linker could be varied, (Fig. 3.5). It would be expected that by increasing the linker length

from C2-, C4- to C6- the T_g values of the materials derived from them should decrease.

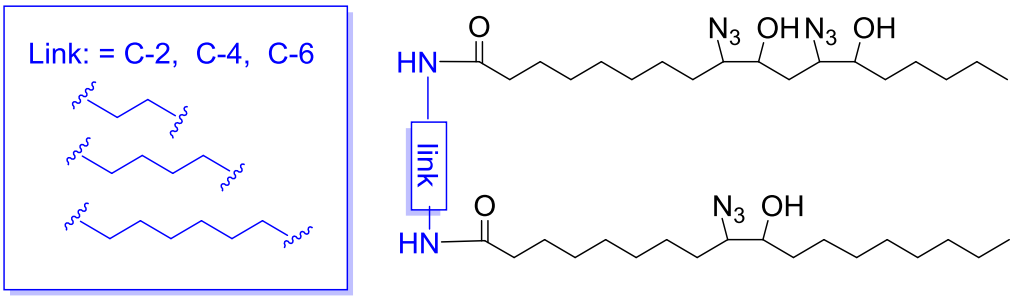


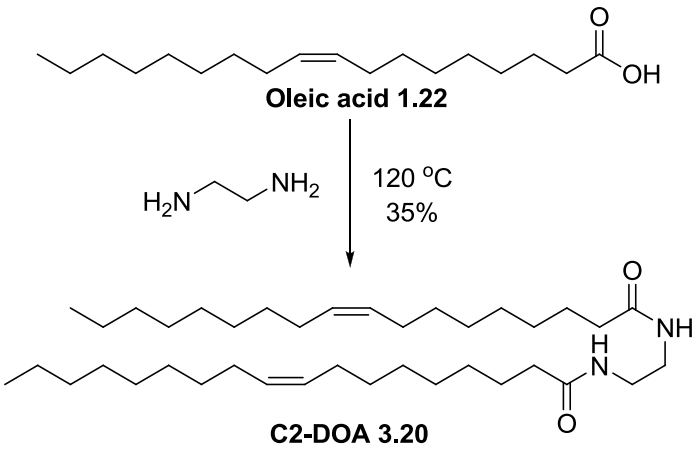
Figure 3.5: Azidated vegetable oil derived diamides with varying linkers.

- Six monomers were prepared from oleic **1.22** and linoleic acids **1.23** to determine the effect of the number of azide groups upon polymer properties (2 oils, 3 linkers).
- Six monomers were also prepared from the triglycerides, rapeseed and soybean oils (2 oils, 3 linkers). The triglyceride oils are cheaper than purified fatty acids and are thus more likely to be used commercially as renewable feedstocks. Rapeseed oil was chosen as it is mainly made up of oleic acid **1.22** residues (61 %) while soybean oil is mainly linoleic **1.23** residues (56 %). Thus, the use of oleic **1.22** and linoleic **1.23** fatty acids should act as good models for the triglycerides themselves.
- Polymerisation reactions of the 12 monomers (4 oils, 3 linkers) were investigated and thermal and mechanical properties measured to determine the effect that increasing the cross-linking (azide value) and monomer length (linker) had on their physical properties.

3.3 Synthesis of C2- linked Amide Click Polymers

3.3.1 Synthesis of C2- linked azido dioleamide (3.22)

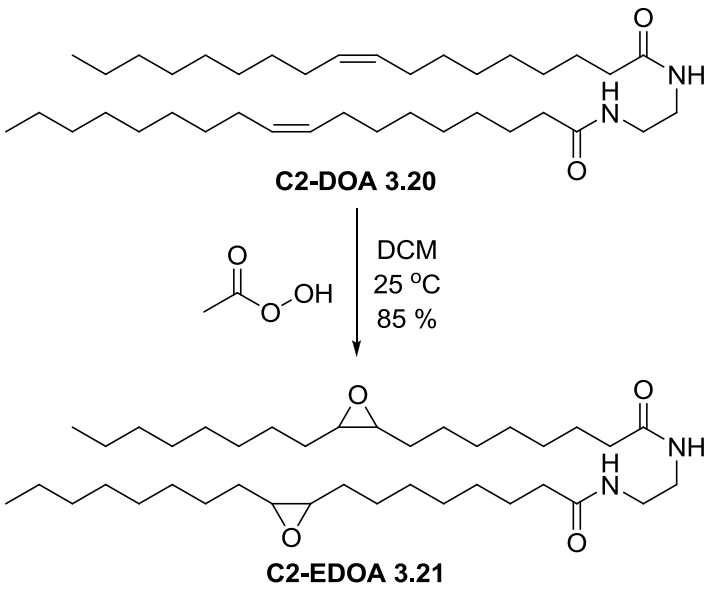
The simplest azide monomer, potentially containing two azide units on average was prepared from oleic acid **1.22**. Oleic acid **1.22** is an 18 carbon chain fatty acid with a single *cis* unsaturation between C9 and C10, (Fig. 3.4). The initial step was the formation of the diamide **3.20**. This was achieved *via* a condensation reaction between oleic acid **1.22** and ethylenediamine at 120 °C overnight, (Scheme 3.2). Purification afforded C2-linked dioleamide derivative C2-DOA **3.20** in a 35 % yield.



Scheme 3.2: Synthesis of C2-DOA 3.20.

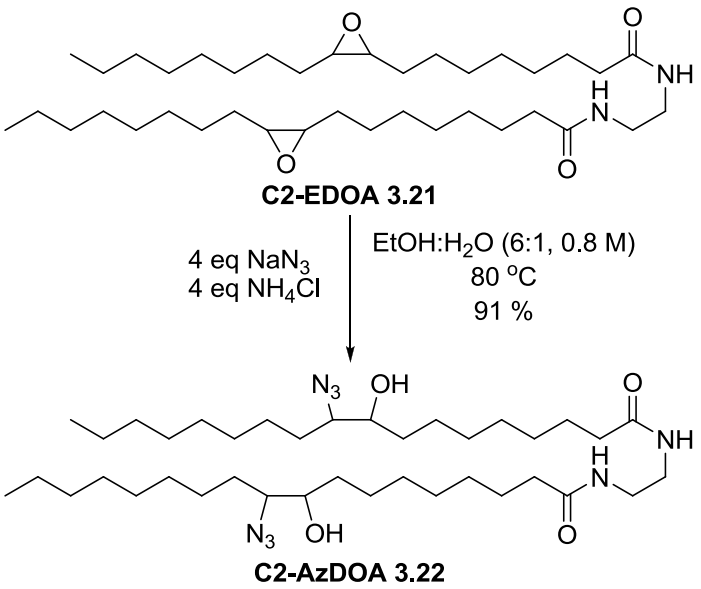
Epoxidation of C2-DOA **3.20** was slightly more problematic. While epoxidation using Venturello's catalyst[89] or *via* the Amberlite® reaction,[93] as described in chapter 2, failed with only recovered starting material being isolated, it was possible to prepare epoxide C2-EDOA **3.21** in 88 % yield in 30 minutes using mCPBA. However, this reaction was only satisfactory on a small scale due to cost implications. On a large scale a more satisfactory procedure was developed using 2.5 equivalents of the cheaper peracetic acid (Scheme 3.3). Although the reaction

was much slower (roughly four times slower), the C2-linked epoxidised dioleamide product C2-EDOA **3.21** was easier to purify by this protocol due to the ease of removing the by-product acetic acid as compared to benzoic acid.



Scheme 3.3: Epoxidation of C2-DOA 3.20 to give C2-EDOA 3.21.

Incorporation of azides into fatty acid epoxides was first achieved in 2008 by Biswas *et al*. however their method used ionic liquids and the conversion rates were slow, taking up to 12 days to achieve full conversion even at 65 °C.[196-197] This was not ideal, therefore an alternative method was required. Various approaches were attempted, such as ring opening of C2-EDOA **3.21** with hydrobromic acid followed by substitution with sodium azide, and the use of Lewis acids to activate the epoxide; however these also didn't achieve full conversion.[198-199] Instead the use of sodium azide in an ethanol: water mixture with ammonium chloride at 80 °C furnished the C2-linked azido dioleamide C2-AzDOA **3.22** in full conversion and in 91 % yield after 8 hours.



Scheme 3.4: Ring opening of C2-EDOA 3.21 with sodium azide.

For the rest of this chapter a bespoke nomenclature system will be adopted to help the reader easily identify the molecules being described in the text. The last two or three letters refers to the starting material (e.g. OA = oleic acid, LA = linoleic acid, RSA = rapeseed derived acids, SBA = soybean derived acids), while the first 2 digits represent the linker length (C2-, C4- or C6-). The remaining characters refer to different stages in the synthesis of the compounds (D = diamide, ED = epoxidised diamide, AzD = azidated diamide). Thus C2-AzDOA refers to the C2-linked azidated dimeric amide derived from oleic acid **3.22**, (Scheme 3.4). As an illustration an example of all the 12 abbreviations required for the C2-series of molecules is shown in Table 3.3. Polymers produced using Cu catalysis or *via* heating (thermal) will be given the abbreviation P^{Cu} and P^{T} respectively.

Oil	Dimeric amide (D)	Epoxide (E)	Azide (Az)
Oleic (OA)	C2-DOA **3.20**	C2-EDOA **3.21**	C2-AzDOA **3.22**
Linoleic (LA)	C2-DLA **3.23**	C2-EDLA **3.24**	C2-AzDLA **3.25**
Rapeseed (RSA)	C2-DRSA **3.35**	C2-EDRSA **3.37**	C2-AzDRSA **3.39**
Soybean (SBA)	C2-DSBA **3.36**	C2-EDSBA **3.38**	C2-AzDSBA **3.40**

Table 3.3: Compound nomenclature and abbreviations.

The 400 MHz ^{1}H NMR for compounds **3.20-3.22**, (Fig. 3.6) clearly illustrate the change in functionality from unsaturated oleamide C2-DOA **3.20** through to epoxidised oleamide C2-EDOA **3.21** and azidated oleamide C2-AzDOA **3.22,** (**Figure 3.6**). The alkene protons in dimer C2-DOA **3.20** can clearly be seen at 5.34 ppm. Upon epoxidation these protons signals shift to 2.90 ppm as they are now part of the epoxide functional group. Ring opening with sodium azide again causes a shift in the protons, one at 3.19 ppm for the proton attached to the carbon with the azide functionality and the other at 3.55 ppm for the proton attached to the hydroxyl group.

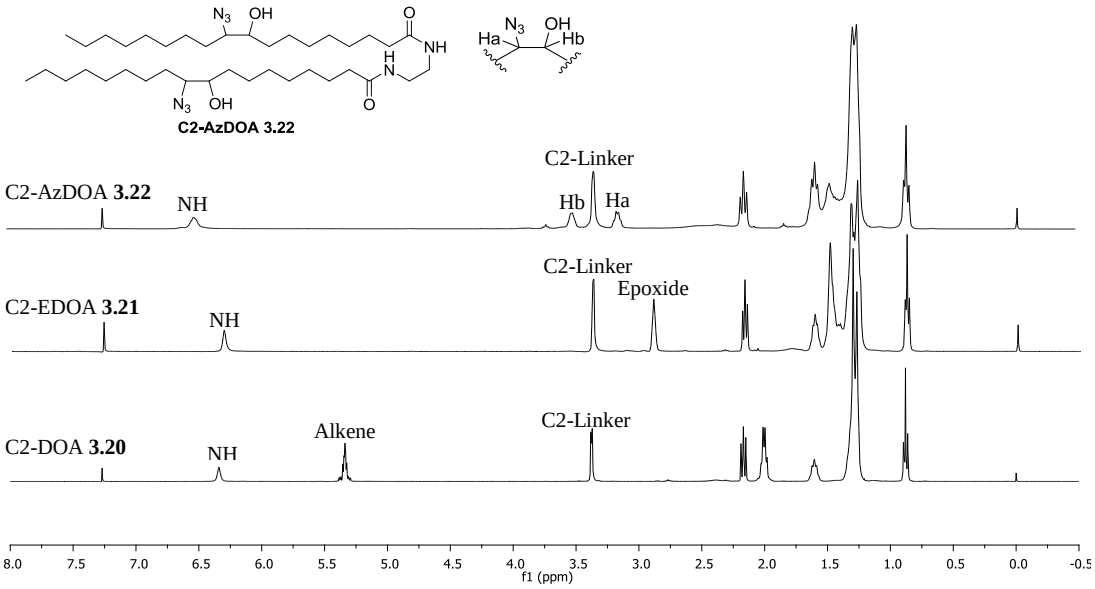


Figure 3.6: 400MHz ^{1}H NMR comparing C2-DOA 3.20, C2-EDOA 3.21 and C2-AzDOA 3.22.

3.3.2 Synthesis of C2 linked monomer C2-AzDLA 3.25

In order to compare how cross-linking density in the final click polymers affects properties it was necessary to prepare a monomer with greater azide functionality. The next simplest unsaturated fatty acid is linoleic acid (Figure 3.4), however pure linoleic acid is expensive, therefore for all further experiments described in this thesis the cheaper technical grade was used (obtained from Sigma Aldrich, containing 60 % linoleic acid, the rest being comprised of primarily of oleic acid). The monomer C2-AzDLA **3.25** was prepared using the same procedure previously described for the oleic acid series, (section 3.3.1) to give C2-DLA **3.23**, C2-EDLA **3.24** and C2-AzDLA **3.25** in 33 %, 81 % and 88 % yields respectively (Fig. 3.7). Five equivalents of peracetic acid were used for the epoxidation process **3.23** → **3.24** and 6 equivalents of sodium azide were used for the azidation reaction **3.24** → **3.25**.

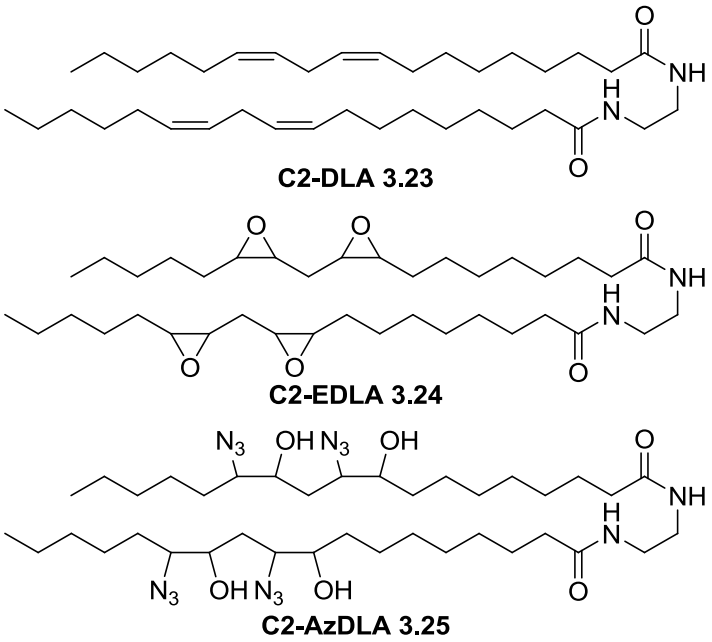


Figure 3.7: Simplified structures of C2-DLA 3.23, C2-EDLA 3.24 and C2-AzDLA 3.25.

Due to the technical grade nature of the linoleic acid used in this study, the exact composition of the C2-AzDLA **3.25** is different to the simplified structure shown in Figure 3.7. Statistically, there will also be a percentage of dimer that has one oleic and one linoleic side chain attached (approx. 48%) and an even smaller percentage that contains two oleic acid side-chains (approx. 16 %). However, to prevent confusion the structures will be drawn as **3.25** and referred as C2-AzDLA throughout this chapter. Mass spectrometry shows the effect of the statistical mixture of the linoleic acid (Fig 3.8b) when compared to oleic (Fig 3.8a), mass ion peaks can clearly be seen for diamides with two oleic chains (729.5 $[M+Na]^+$ (2 x C18:1)), one oleic and one linoleic (786.5 $[M+Na]^+$ (C18:2, C18:1)). and two linoleic chains (843.5 $[M+Na]^+$ (2 x C18:2))

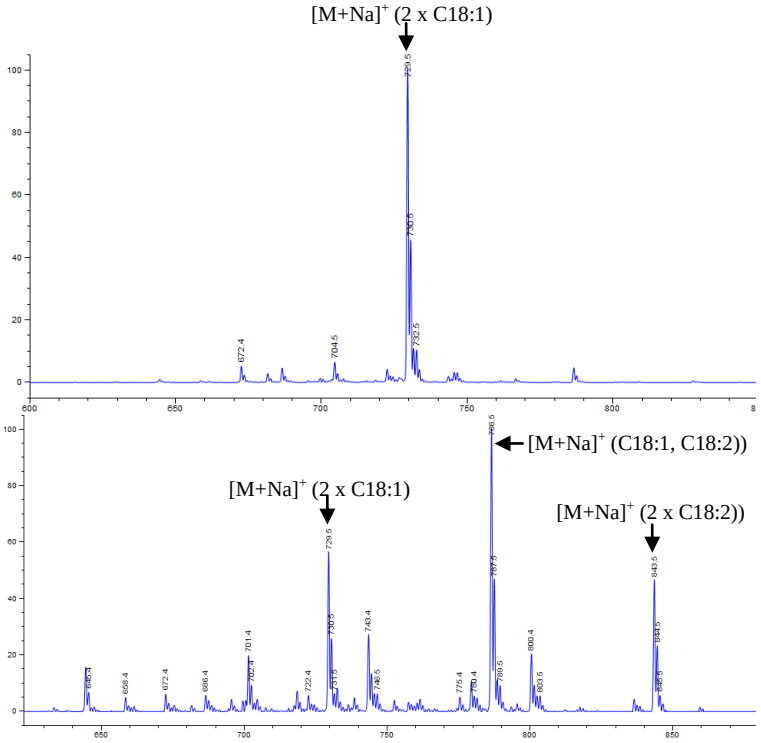


Figure 3.8: Mass spectra of (a) C2-AzDOA 3.22 and (b) C2-AzDLA 3.25

3.3.3 Thermal analysis of C2-ADOA 3.22 and C2-AzDLA 3.25

Both monomers C2-AzDOA **3.22** and C2-AzDLA **3.25** were subjected to TGA and DSC analysis. This was to better understand their thermal properties prior to being incorporated into a polymer (Table 3.4). The TGA (Fig. 3.9) shows a two-step degradation process for both monomers, there is an initial degradation at around 220 °C with a mass drop of 10 % up to 250 °C, which implies it is the thermal degradation of the azide groups present in the monomers.[200] The secondary degradation starts at around 300 °C and continues until both monomers are fully degraded.[112]

Monomer	TGA (°C)			DSC (°C)	
	$T_{10\%}$	$T_{50\%}$	T_{max}	T_g	MPt
C2-AzDOA **3.22**	244	429	499	-21	79
C2-AzDLA **3.25**	231	402	495	-5	78

[a] DSC and TGA values measured using 10 °C /min.

Table 3.4: Thermal data comparison.

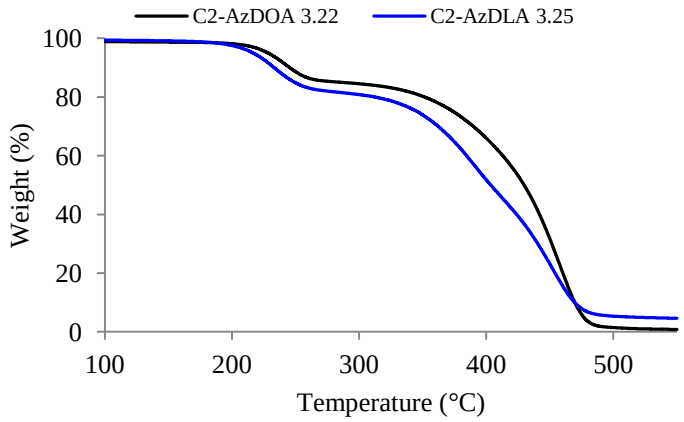


Figure 3.9: TGA of C2-ADOA 3.22 and C2-ADLA 3.25 monomers.

The higher T_g for C2-AzDLA **3.25** at -5 °C compared to C2-AzDOA **3.22** at -21 °C is expected for a compound with more azide groups. As each azide group is added an additional hydroxyl group is unmasked allowing a higher level of H-bonding between molecules.

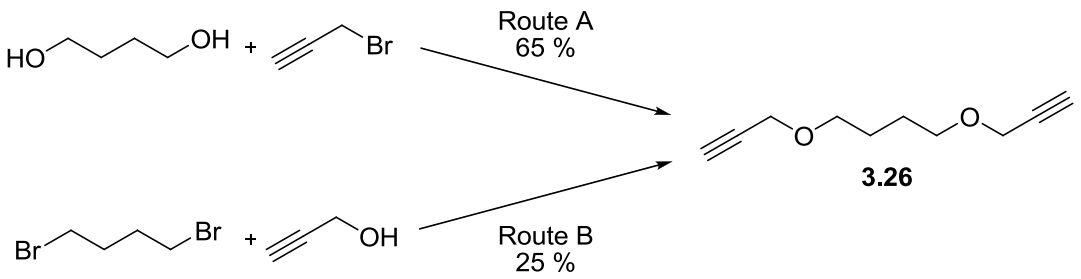
The azide functionality % (N_f) was calculated using equation 3.1 below where Mw = molecular weight, nitrogen content was determined by elemental analysis and 42 is the mass of the azide group.

$$N_f = \frac{Mw \times (nitrogen\ content)}{42 \times 100} \quad (Equation\ 3.1)$$

C2-AzDOA **3.22** was found to contain only 1.7 azide groups and C2-AzDLA **3.25** contained 2.3 azide groups on average. This information was then used to determine the amount of dialkyne required for polymerisation.

3.3.4 Synthesis of 1,4-bis(propynyloxy) butane linker 3.26.

In order to polymerise the two C2-azide monomers *via* click chemistry, a dialkyne unit is required as a second monomer. A flexible linker **3.26** was chosen. The preparation of the dialkyne unit **3.26** was achieved by two methods (Scheme 3.5). Both routes were similar, in that an alcohol was deprotonated with sodium hydride to produce an alkoxide which underwent a S_N2 reaction with an appropriate alkyl halide to produce **3.26**. While both approaches were successful, route B was lower yielding and therefore route A was the preferred method. Route A is also preferred on sustainability grounds as it uses the renewable diol, 1,4-butane diol as a starting material.[201]



Scheme 3.5: Two possible synthetic routes to linker 3.26.

Thermal analysis of **3.26** showed there was only one major decomposition pathway occurring at 235 °C, however the linker begins to degrade slowly from 150 °C indicating the highest temperature range applicable for its use in any thermal mediated click reaction (Fig. 3.10).

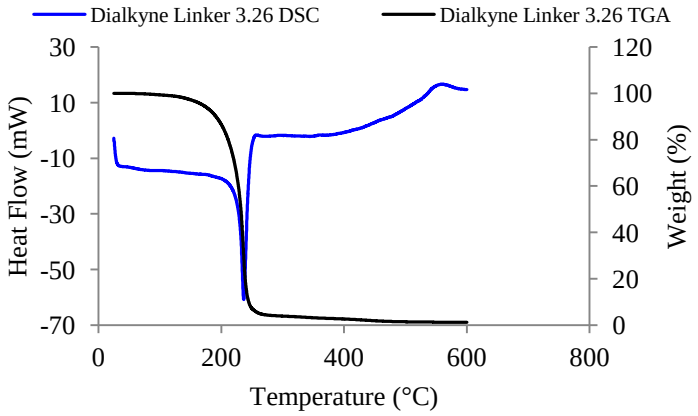
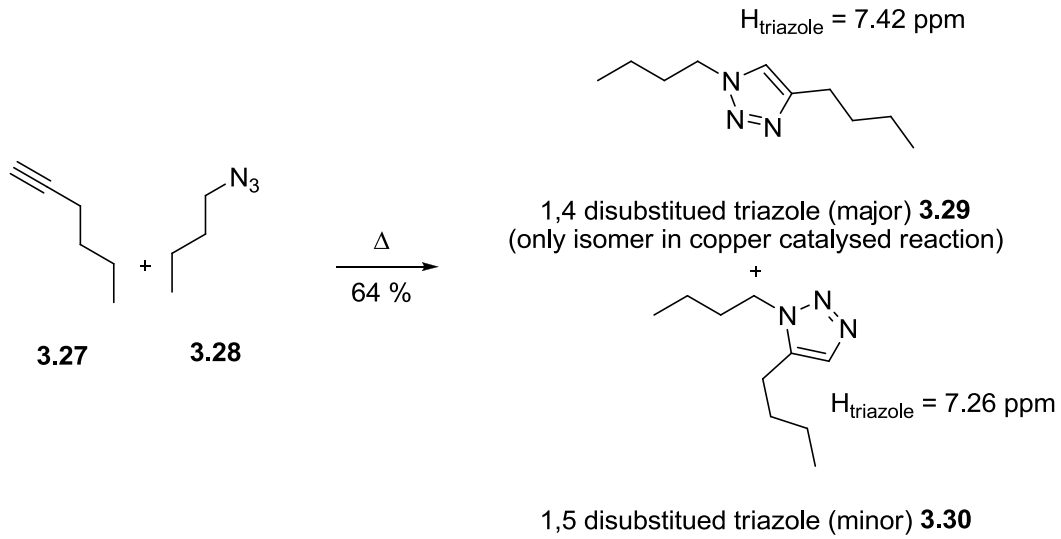


Figure 3.10: Combined TGA DSC of dialkyne linker 3.26.

3.3.5 Polymerisation of C2-AzDOA 3.22 and C2-AzDLA 3.25 with dialkyne 3.26 *via* copper catalysed click reaction.

C2-AzDOA **3.22** and C2-AzDLA **3.25** were polymerised *via* copper catalysed click chemistry. This was achieved using $CuSO_4$ pentahydrate and sodium ascorbate in a THF: water (5:1) solvent mix. The reaction was carried out at room temperature so

that no thermal degradation would occur. Literature precedence indicates that copper catalysed reactions normally proceed to give one isomer of the 1,2,3-triazole due to the involvement of a terminal copper acetylene complex and the orientation in which the azide complexes with the copper during the catalytic cycle.[202] Both possible isomers can be easily identified by the characteristic ^{1}H NMR shifts of their triazole protons, (Scheme 3.6).

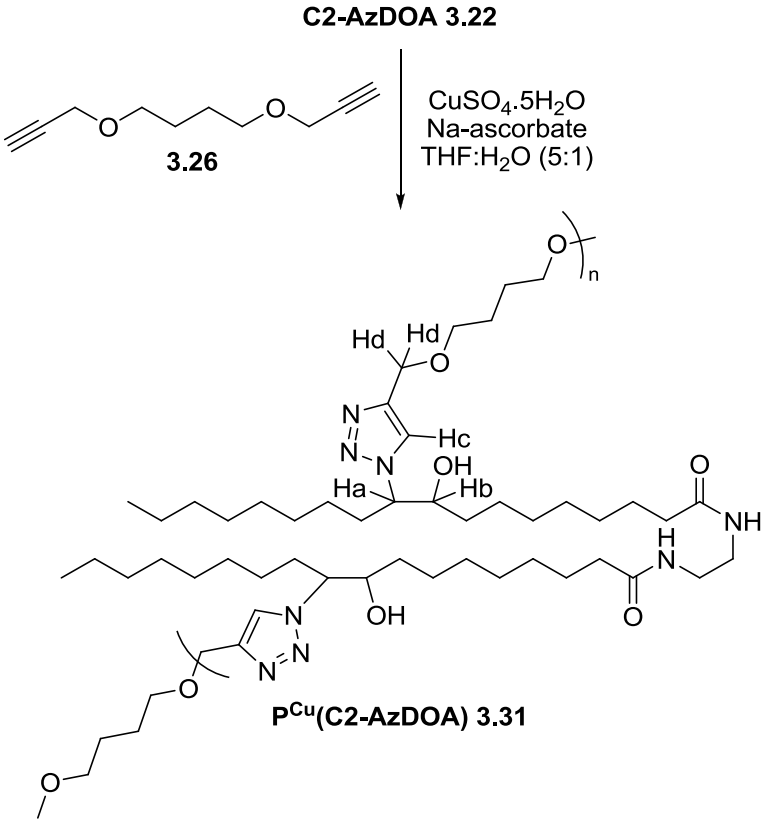


Scheme 3.6: Simple azide reaction showing both possible isomers.[203]

Linoleic polymerisation passed the gelation point within 30 minutes as evident with the C2-AzDLA monomer **3.25** forming a gelled material P^{Cu}(C2-AzDLA) **3.32** (Scheme 3.7). P_{gel} value, calculated using equation 3.2 where f = mean number of functional groups per monomer, of the systems is 0.87 therefore showing 87 % of monomers had reacted. Oleic monomers never passed gelation point and had Pgel values of 1.

$$P_{gel} = \frac{1}{(f-1)} \qquad (Equation\ 3.2)$$

The polymers were dried in a 30 °C oven over night and then subjected to thermal analysis. Reaction with the linoleic derivative, C2-AzDLA monomer **3.25** (2.3 azide groups on average) produces an insoluble material P^{Cu}(C2-AzDLA) **3.32** while the oleic derivative, C2-AzDOA **3.22** (1.7 azide groups on average) produces an organic soluble polymer P^{Cu}(C2-AzDOA) **3.31**. The 400 MHz ^{1}H NMR (Fig 3.11) of this soluble material **3.31** confirms that polymerisation has occurred (due to the broadening of the peaks) and also shows a single peak at 7.78 ppm which corresponds to the previously mentioned 1,4-disubstituted 1,2,3-triazole isomer. The dialkyne linker can be seen at 3.51 ppm and 1.64 ppm also confirming incorporation. GPC analysis proves C2-AzDOA **3.22** gives low MWt polymers with a weight average MWt (Mw) of 4239 and a polydispersity of 1.10.



Scheme 3.7: Copper catalysed polymerisation reaction.

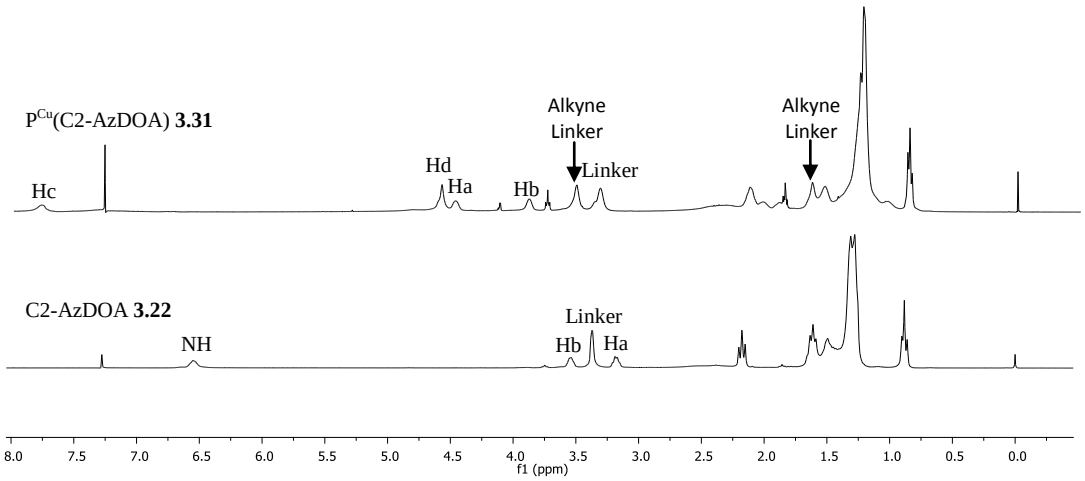


Figure 3.11: 400MHz ^{1}H NMR spectrum comparing C2-ADOA 3.22 and P^{Cu}(C2-AzDOA) 3.31.

3.3.6 Thermal analysis of P^{Cu}(C2-AzDOA) 3.31 and P^{Cu}(C2-AzDLA) 3.32.

Entry	TGA (°C)[a]			DSC (°C)[a]
	T_{10}	T_{50}	T_{max}	T_g
C2-AzDOA **3.22**	244	429	429	-21
C2-AzDLA **3.25**	231	402	402	-5
P^{Cu}(C2-AzDOA) **3.31**	271	396	481	-13
P^{Cu}(C2-AzDLA) **3.32**	301	396	483	23

[a] DSC and TGA values measured using 10 °C /min

Table 3.5: Comparison of thermal properties between monomers and polymers.

DSC analysis shows the T_g's have increased upon polymerisation (Table 3.5). For the oleic acid derivatives (**3.22** → **3.31**) it has increased by 8 °C, while for the linoleic derivatives (**3.25** → **3.32**) the increase is greater at 28 °C, and this is a reflection on the increased cross-linking due to the increased azide functionality. In addition, it is likely that residual copper could be trapped within the polymer network in the linoleic series, making the polymer more brittle and increasing the T_g further. This effect was not present in P^{Cu}(C2-AzDOA) **3.31** as it was soluble in

organic solvents and the $CuSO_4$ phase separated and formed a layer on the bottom of the vial when the polymer was dried.

TGA analysis (Fig 3.13) shows a much wider decomposition range for the polymers than the monomers. The most noticeable difference is the absence of the mass drop between 200 °C and 260 °C indicating that all the azide groups have reacted. There is a small weight drop of 5 % present in P^{Cu}(C2-AzDOA) **3.31** which is believed to be due to residual solvent from the polymerisation reaction. Infra-red analysis shows the azide stretch at 2100 cm^{-1} in the C2-AzDOA monomer **3.22** and its absence in the polymer P^{Cu}(C2-AzDOA) **3.31**, (Fig. 3.12).

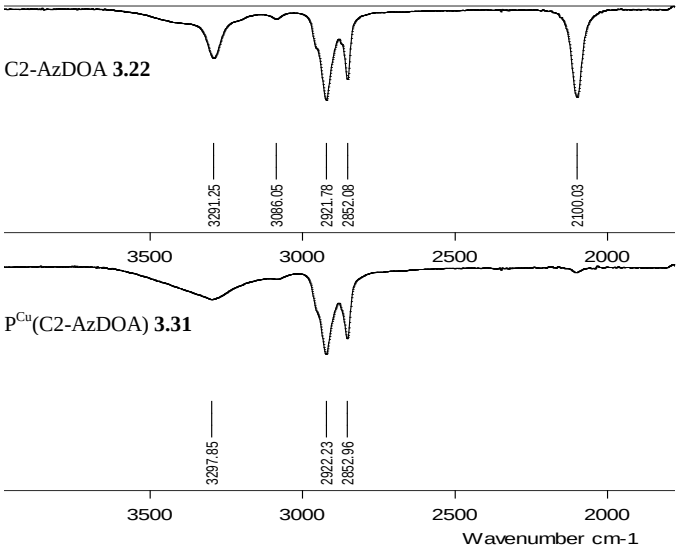


Figure 3.12: IR spectra of C2-AzDOA 3.22 and P^{Cu}(C2-AzDOA) 3.31.

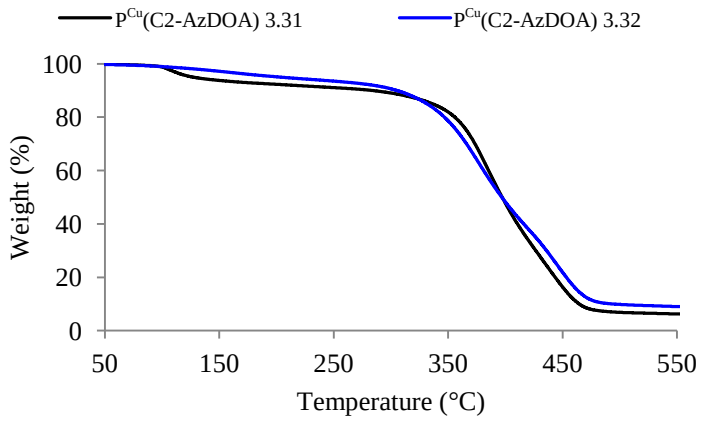


Figure 3.13: TGA of P^{Cu}(C2-ADOA) polymer 3.12 and P^{Cu}(C2-ADLA) polymer 3.13.

The $T_{10\%}$, $T_{50\%}$ and T_{max} show that both the polymers P^{Cu}(C2-AzDOA) **3.31** and P^{Cu}(C2-AzDLA) **3.32** are initially more thermally stable than their corresponding monomers C2-AzDOA **3.22** and C2-AzDLA **3.25** however the T_{50} mark is much lower for P^{Cu}(C2-AzDOA) **3.31** (ΔT_{50} = -33°C) with less of a difference for P^{Cu}(C2-AzDLA) **3.32** (ΔT_{50} = -6°C).

3.3.7 Synthesis of C2-monomers from rapeseed and soybean oils.

Having successfully polymerised both the oleic and linoleic derived materials the next stage was to attempt to make similar analogues derived from renewable triglyceride oils. Triglycerides are generally cheaper renewable starting materials than the more purified fatty acids and thus are more likely to be used as industrial feedstocks. However, triglyceride oils are not homogenous materials and thus the materials properties from polymers prepared from them are more varied. The two oils chosen were rapeseed oil and soybean oil. These two oils were chosen as they are commercially available in bulk at low prices and due to the similarity of their fatty acid composition with C2-AzDOA **3.22** and C2-AzDLA **3.25** (rapeseed contained 60.5% oleic acid) and soybean oil contained 57.7% linoleic acid), Table

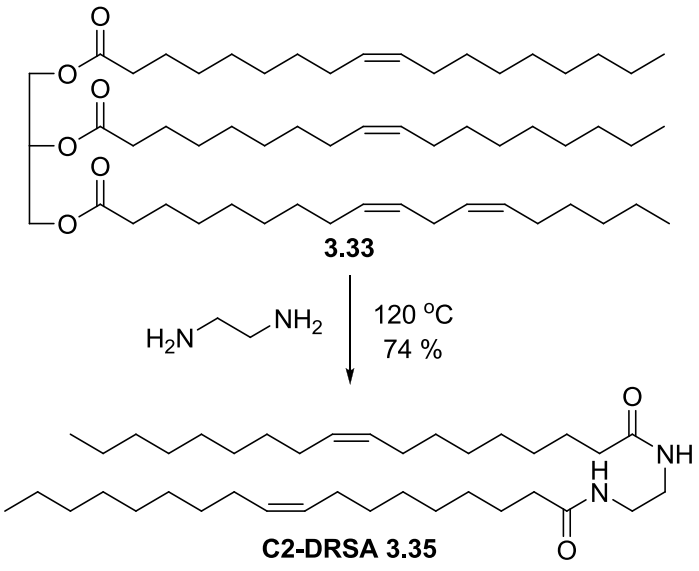
3.6. The hypothesis was that polymers from rapeseed should resemble those from C2-AzDOA **3.31** while those from soybean oil should resemble those from C2-AzDLA **3.32**. The fatty acid composition was determined by FAME analysis for the two oils and is shown in Table 3.6.

	Rapeseed Oil[a]	Soybean Oil[a]
Saturated Fatty Acid	6.7 %	17.2 %
Oleic Acid	60.5 %	24.8 %
Linoleic Acid	31.1 %	57.7 %

[a] Determined by FAME analysis.

Table 3.6: Fatty Acid composition of rapeseed oil and soybean oil.

The first step in the synthesis was aminolysis of the triglycerides rapeseed **3.33** and soybean **3.34** with the ethylenediamine (Scheme 3.8). This has been achieved previously in by using a catalytic amount of sodium methoxide at 120 °C. However, it was not necessary to include this reagent (thus decreasing the cost of the procedure) and instead the desired products C2-DRSA **3.35** and C2-DSBA **3.36** were prepared following the same procedure used to synthesise **3.20** in 74 % and 62 % yields respectively.



Scheme 3.8: Aminolysis of triglycerides.

Epoxidation of the rapeseed oil diamide C2-DRSA **3.35** and soybean oil diamide C2-DSBA **3.36** was achieved using the same approach as C2-EDOA **3.21** and C2-EDLA **3.24** using 5 equivalents of peracetic acid for full epoxidation. Likewise azidation was achieved using the same procedure as described for the synthesis of C2-AzDOA **3.22** to afford the two vegetable oil based monomers C2-AzDRSA **3.39** and C2-AzDSBA **3.40** in 90 % and 98 % yield respectively. Mass spectrometry C2-AzDRSA **3.39** (Fig 3.14) shows a major peak for two oleic side chains and compares with the oleic monomer, however it also shows presence of one oleic and one linoleic and a very small amount of 2 linoleic side chains which is to be expected as rapeseed oil contains 31 % linoleic acid. Small percentages of saturated side chain can also be seen between 644.4 and 722.4. C2-AzDSBA **3.40** (Fig 3.15) shows a higher amount of saturated fatty acid as evident from the FAME analysis showing 17 % saturated fatty acid. The peak at 701.4 shows that actually C17 is present in the oil as the mass ion peak is equivalent to 2 x C17:1 with azide groups present. Again mass ion peaks of 786.5 and 843.5 are present showing C18:1,C18:2 and 2 x C18:2 side chained fatty amides respectively.

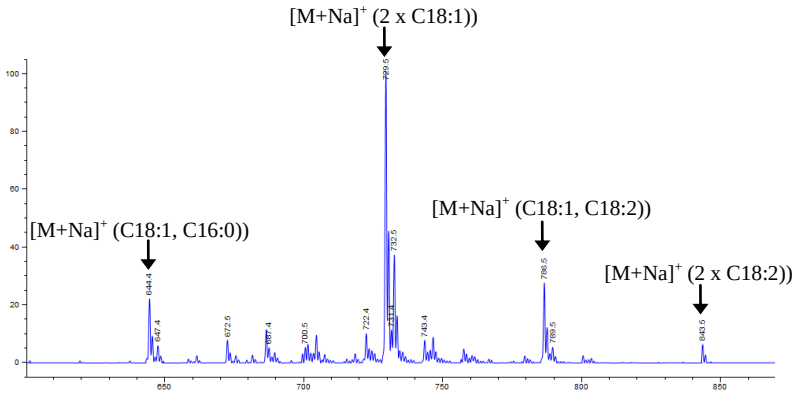


Figure 3.14: Mass spectrum of C2-AzDRSA 3.39

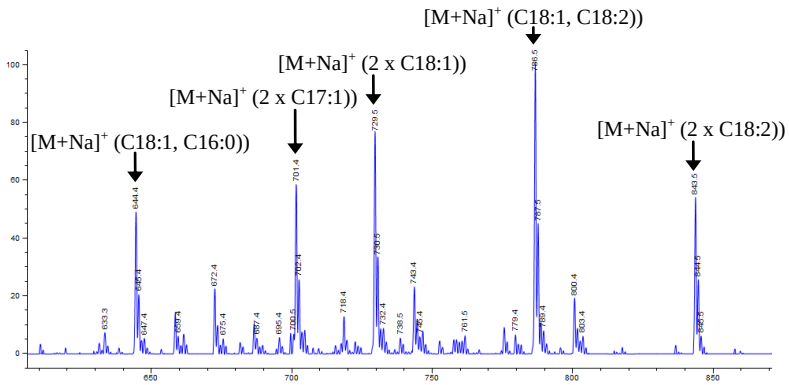


Figure 3.15: Mass spectrum of C2-AzDSBA 3.40.

3.3.8 Thermal analysis of C2-AzDRSA 3.39 and C2-AzDSBA 3.40.

As for the other oleic and linoleic derived monomers, C2-AzDRSA **3.39** and C2-AzDSBA **3.40** were subjected to thermal analysis Fig 3.16). The same initial two-step degradation, caused by the decomposition of the azide groups as seen in C2-AzDOA **3.22** and C2-AzDLA **3.25**, was seen in these monomers. C2-AzDRSA **3.39** has a slightly higher thermal stability than C2-AzDSBA **3.40**, this mirrors that observed with the oleic C2-AzDOA **3.22** and linoleic C2-AzDLA **3.25** showing that the monomer in each series with the highest levels of chains derived from linoleic fatty acid residues is the less thermally stable. Based upon this conclusion (and the relative ratios of oleic or linoleic acids derived from the triglycerides) one would predict a decreasing thermal stability in the series C2-AzDOA > C2-AzDRSA > C2-AzDLA ~ C2-AzDSBA.

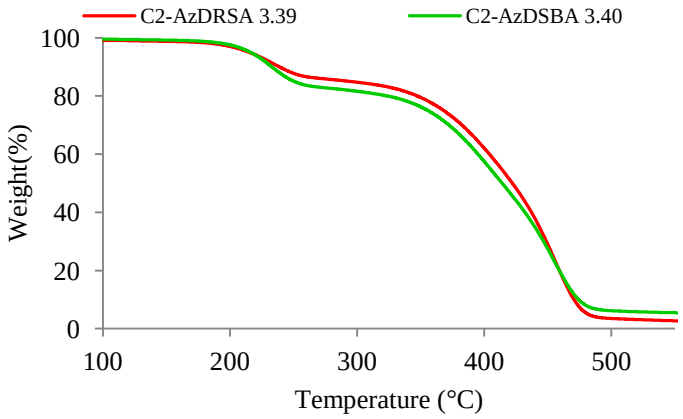


Figure 3.16: TGA of C2-AzDRSA (3.39) and C2-AzDSBA (3.40) monomers.

The values of $T_{10\%}$, $T_{50\%}$ and T_{max} for all four monomers (Table 3.7) show that C2-AzDOA **3.22** is indeed the most thermally stable up to 50 % degradation. C2-AzDRSA **3.39** is the next most stable due to the amount of linoleic moiety present being lower than C2-AzDLA **3.25** and C2-AzDSBA **3.40**. C2-AzDLA **3.25** and C2-AzDSBA **3.40** have very similar thermal stability due to the amount of linoleic moiety being similar in both compounds, but the $T_{50\%}$ is different due to the amount of unsaturated fatty acid in the soybean triglyceride derivative C2-AzDSBA **3.40** being higher than in C2-AzDLA **3.25**. All T_{max} values are within 10 °C showing that all the monomers are fully degraded to black char around the same temperature.

Monomer	TGA (°C)[a]			DSC (°C)[a]	
	$T_{10\%}$	$T_{50\%}$	T_{max}	T_g	MPt
C2-AzDOA **3.22**	244	429	499	-21	79
C2-AzDLA **3.25**	231	402	495	-5	78
C2-AzDRSA **3.39**	236	421	500	-8	78
C2-AzDSBA **3.40**	231	413	491	-9	78

[a] DSC and TGA values measured using 10 °C /min.

Table 3.7: Thermal data of all four C2 monomers.

DSC analysis shows the T_g of the two triglyceride based monomers C2-AzDRSA **3.39** and C2-AzDSBA **3.40** are similar to each other (-8°C and -9°C respectively) and resemble that of the linoleic fatty acid derivative C2-AzDLA **3.25** (-5°C) more than the oleic derivative C2-ADOA **3.22** (-21°C) (Fig. 3.17). This is to be expected as both the triglyceride derived monomers C2-ADRSA **3.39** and C2-ADSBA **3.40** have significant amounts of linoleic acid derived side-chains. However, the fact that both triglyceride derivatives have similar values despite the significant difference in the amount of initial linoleic acid content (C2-AzDRSA **3.39** = 31% and C2-ADSBA **3.40** = 58% respectively) is more puzzling. While the presence of linoleic derived side chains will increase the T_g (more hydroxyl groups to H-bond) the presence of fully saturated side chains will lower it. C2-AzDSBA **3.40**, while it has significantly more linoleic acid derived residues, also has significantly more saturated fatty acid components (17%) than C2-AzDRSA **3.39** (7% respectively). These two different factors oppose each other and hence the T_g values are coincidently similar.

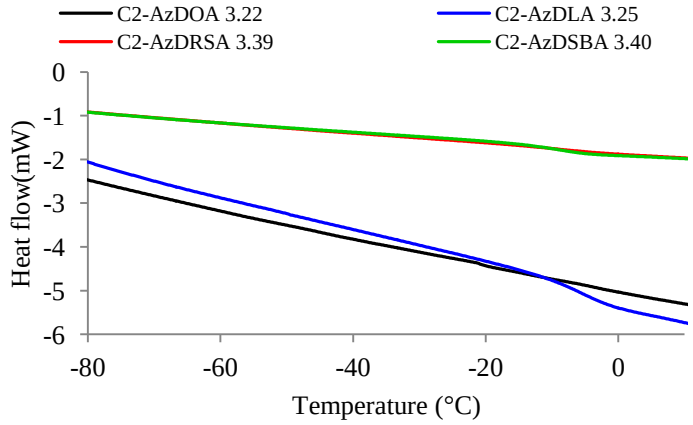


Figure 3.17: DSC of C2-AzDOA 3.22, C2-AzDLA 3.25, C2-AzDRSA 3.39, and C2-AzDSBA 3.40.

The azide functionality was calculated for both the triglyceride derived monomers C2-AzDRSA **3.39** and C2-AzDSBA **3.40** and these were compared to C2-AzDOA

3.22 and C2-AzDLA **3.25**. The results can be seen in table 3.8. As a consequence, it can be predicted that the thermal properties of click polymers derived from C2-AzDOA **3.22** and C2-AzDRSA **3.39** might be similar as would those from C2-AzDLA **3.25** and C2-AzDSBA **3.40**.

Monomer	Azide Functionality[a]
C2-ADOA **3.22**	1.7
C2-ADLA **3.25**	2.3
C2-ADRSA **3.39**	1.6
C2-ADSBA **3.40**	2.2

[a] Number of the azide groups (Nf) per monomer was calculated using the equation: Nf = (Mn × nitrogen content)/(molecular mass of the azide group×100).

Table 3.8: Azide functionality of C2 monomers.

3.3.9 Copper catalysed polymerisation of C2-AzDRSA 3.39 and C2-AzDSBA 3.40.

Polymerisation was achieved using the same protocol as for C2-AzDOA **3.22** and C2-AzDLA **3.25**. As before the reaction formed a gel in 30 minutes to give the desired polymers P^{Cu}(C2-AzDRSA) **3.41** and P^{Cu}(C2-AzDSBA) **3.42**. Pgel calculations give values of 0.91 showing 91 % conversion of monomers at gel point. Due to the presence of linoleic acid derived side-chains both polymers are cross-linked and insoluble in organic solvents, as a result we did not obtain ^{1}H NMR data and so it was not possible to confirm that the click polymerisation proceeded to give one regioisomer only. Interestingly 87 % and 91 % conversion was required for the two monomers with highest linoleic acid content (C2-AzDLA **3.25**) and (C2-AzDSBA **3.40**) showing it takes a large amount of conversion to form a gel, which would explain why C2-AzDRSA **3.39** only formed insoluble polymers after the

solvent had been removed as the percentage of linoleic is approximately half that of C2-AzDLA **3.25**.

3.3.10 Thermal analysis of P^{Cu}(C2-AzDRSA) 3.41 and P^{Cu}(C2-AzDSBA) 3.42.

Entry	TGA (°C)[a]			DSC (°C)[a,b]	linoleic
	T_{10}	T_{50}	T_{max}	T_g	%[c]
P^{Cu}(C2-AzDOA) **3.31**	271	396	481	-13 (-21)	0
P^{Cu}(C2-AzDLA) **3.32**	301	396	483	23 (-5)	60
P^{Cu}(C2-AzDRSA) **3.41**	311	400	485	-2 (-8)	31
P^{Cu}(C2-AzDSBA) **3.42**	309	396	486	25 (-9)	58

[a] DSC and TGA values measured using 10 °C /min. [b] Values for corresponding monomers in brackets. [C] Determined by FAME analysis.

Table 3.9: Thermal data of the C2 copper.

As previously described in section 3.3.6, the glass transition temperature (T_g) for both triglyceride polymers increased relative to their monomers (Table 3.9). For rapeseed P^{Cu}(C2-AzDRSA) **3.41** the increase was similar to the oleic derived material (compare P^{Cu}(C2-AzDRSA) **3.41** ΔT_g = 6 °C, P^{Cu}(C2-AzDOA) **3.31** ΔT_g = 8 °C), and for the soybean P^{Cu}(C2-AzDSBA) **3.42** it was much higher but similar to the linoleic derived material (compare P^{Cu}(C2-AzDSBA) **3.42** ΔT_g = 34 °C, P^{Cu}(C2-AzDLA) **3.32** ΔT_g = 28 °C). Indeed, the increase in T_g is closely correlated to the % of linoleic side chains within the polymer network (Fig. 3.18). This can be rationalised by examining the level of free chain-length between the triazole and the terminal end of the fatty amide moiety. Those polymers containing an oleic moiety will have a longer terminal alkyl chain after the triazole link than those with increased numbers of linoleic residues, therefore there will be a longer branch per repeat unit lowering the T_g due to less favourable packing of the polymer chains. In addition, the presence of linoleic chains provides cross-linking points, also increasing the T_g.

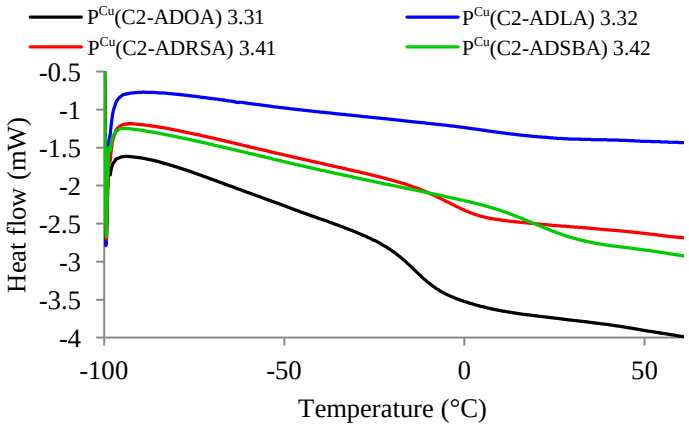


Figure 3.18: DSC of P^{Cu}(C2-AzDOA) 3.31, P^{Cu}(C2-AzDLA) 3.32, P^{Cu}(C2-AzDRSA) 3.41, and P^{Cu}(C2-AzDSBA) 3.42.

As with the analogous polymers derived from oleic and linoleic fatty acids, P^{Cu}(C2-AzDOA) **3.31** and P^{Cu}(C2-AzDLA) **3.32**, the TGA analysis for the polymers derived from the triglycerides P^{Cu}(C2-AzDRSA) **3.41** and P^{Cu}(C2-AzDSBA) **3.42** shows a much wider decomposition range for the polymers compared to their respective monomers (Fig. 3.19). As before, the two-step decomposition pathway of the monomer is not observed and instead the one decomposition pathway proved a large mass drop between 270 °C and 460 °C.

The effect of trapped residual $CuSO_4$ in the polymer network on the thermal properties of the materials was uncertain and hence attention was turned to facilitating the polymerisation thermally without the need for a catalyst. Previous work by Shah *et al.* had shown that thermally mediating the reactions led to materials with a higher thermal stability and we were intrigued to determine if the same would be the case in our polymers.[138]

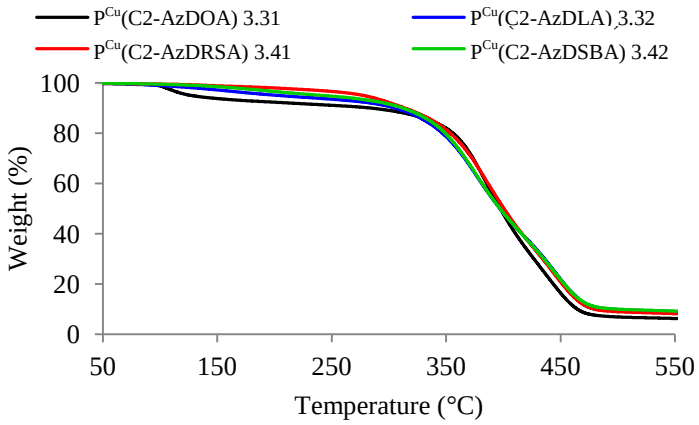


Figure 3.19: TGA of P^{Cu}(C2-AzDOA) 3.31, P^{Cu}(C2-AzDLA) 3.32, P^{Cu}(C2-AzDRSA) 3.41, and P^{Cu}(C2-AzDSBA) 3.42.

3.3.11 Polymerisation of C2-monomers *via* a thermal approach.

Having successfully synthesised the four C2-monomers (C2-AzDOA **3.22,** C2-AzDLA **3.25,** C2-AzDRSA **3.39,** C2-AzDSBA **3.40**) and polymerised them using copper catalysis, the next aim was to polymerise the same monomers without the use of $CuSO_4$ to provide materials suitable for mechanical testing. The four monomers C2-AzDOA **3.22**, C2zADLA **3.25**, C2-AzDRSA **3.39** and C2-AzDSBA **3.40** were dissolved in acetone and the appropriate amount of alkyne **3.26** was added. Each solution was cast into a specially prepared silicone mould preheated to 80 °C. The solutions were maintained at 80 °C until the solvent had evaporated, and then transferred to a vacuum oven at 80 °C (380 mmHg) to ensure all solvent had been removed and to remove any trapped air pockets. The pressure was then returned to atmospheric pressure and the temperature increased to 100 °C for 24 hours. As before the polymer derived from the oleic monomer, P^{T}(C2-AzDOA) **3.43** dissolved in a range of organic solvents and hence a 400MHz ^{1}H NMR could be obtained to determine if the triazole formation during the click process was regioselective (Fig.

3.20). Analysis indicated that unlike the copper catalysed polymerisation, where only one regioisomer of P^{Cu}(C2-AzDOA) **3.31** was formed, the thermal process was less selective, giving rise to a small amount of the minor 1,5-substituted 1,2,3-triazole (2:1 ratio obtained from integration of ^{1}H NMR).

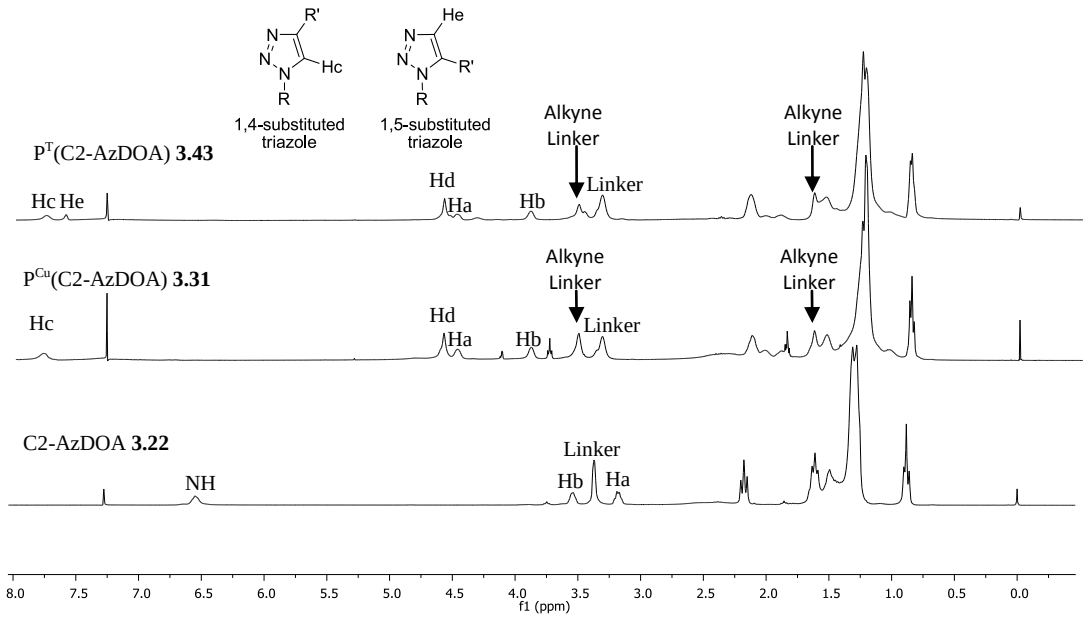


Figure 3.20: 400 MHz ^{1}H NMR spectrum of C2-AzDOA monomer 3.22, and polymers P^{Cu}(C2-AzDOA) 3.31 and P^{T}(C2-AzDOA) 3.43 showing regioselectivity.

3.3.12 Thermal analysis of C2 polymers prepared *via* the thermal method.

As before with the copper catalysed polymerisations, thermal analysis was carried out on the thermally derived polymers in order to establish if there were any significant differences between materials prepared *via* the two different routes. The first major difference of note is that the T_g's for all the thermally derived polymers were significantly higher than those materials prepared using copper catalysis (Fig. 3.21), (oleic polymers P^{T}(C2-AzDOA) T_g = 0 °C > P^{Cu}(C2-AzDOA) T_g = -13 °C; ΔT_g = +13 °C); (linoleic polymers P^{T}(C2-AzDLA) T_g = 35 °C > P^{Cu}(C2-AzDLA) T_g = 23 °C; ΔT_g = +12 °C); (rapeseed polymers P^{T}(C2-AzDRSA) T_g = 15 °C > P^{Cu}(C2-

AzDRSA) T_g = -2 °C; ΔT_g = +17 °C); (soybean oil polymers P^{T}(C2-AzDSBA) T_g = 33 °C > P^{Cu}(C2-AzDSBA) T_g = 25 °C; ΔT_g = +8 °C). This may be due to a) significant metal residues in polymers prepared using copper catalysis, b) better reactivity, degree of polymerisation and cross-linking in thermally derived materials, or c) an artefact of the thermal process being less regioselective. However, the same correlation of increased T_g with the percentage of linoleic derived side-chains is observed for both thermal and copper methods.

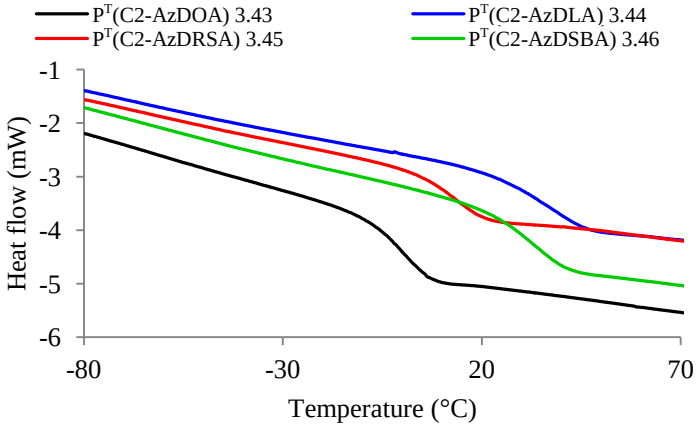


Figure 3.21: DSC of P^{T}(C2-AzDOA) 3.43, P^{T}(C2-AzDLA) 3.44, P^{T}(C2-AzDRSA)3.45, P^{T}(C2-AzDSBA) 3.46.

The thermally derived polymers show a narrower decomposition range compared to the copper catalysed polymers as well as an increased $T_{10\%}$, (Fig 3.22 and 3.23). This follows the same trend seen by Shah *et al*. and was postulated to arise due to "*the cross-linking in polymers obtained thermally is more homogeneous than that in polymers obtained by the CuAAC polyaddition*."[138]

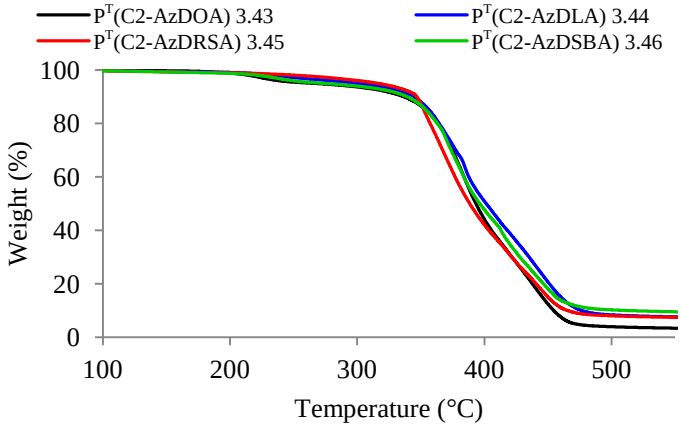


Figure 3.22: TGA of P^{T}(C2-AzDOA) 3.43, P^{T}(C2-AzDLA) 3.44, P^{T}(C2-AzDRSA)3.45, P^{T}(C2-AzDSBA) 3.46.

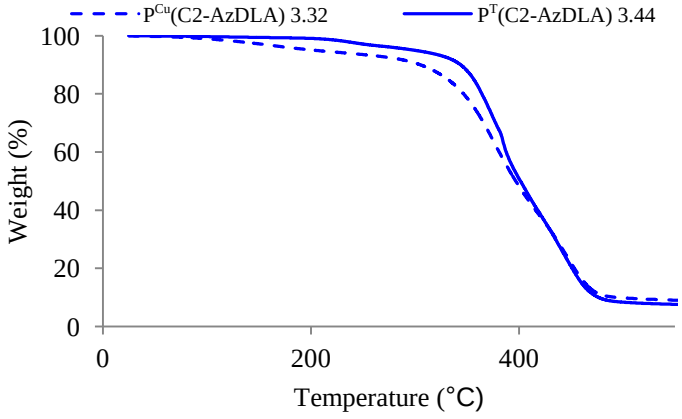


Figure 3.23: Comparison of TGA of P^{Cu}(C2-AzDLA) 3.32 and P^{T}(C2-AzDLA) 3.44.

Entry	TGA (°C)[a]			DSC (°C)[a]
	T_{10}	T_{50}	T_{max}	T_g
P^{Cu}(C2-AzDOA) **3.31**	271	396	481	-13
P^{Cu}(C2-AzDLA) **3.32**	301	396	483	23
P^{Cu}(C2-AzDRSA) **3.41**	311	400	485	-2
P^{Cu}(C2-AzDSBA) **3.42**	309	396	486	25
P^{T}(C2-AzDOA) **3.43**	333	393	478	0
P^{T}(C2-AzDLA) **3.44**	342	396	480	35
P^{T}(C2-AzDRSA) **3.45**	346	388	481	15
P^{T}(C2-AzDSBA) **3.46**	341	400	490	33

[a] DSC and TGA values measured using 10 °C /min.

Table 3.10: Thermal data of all C2 polymers.

The T_{10} values for the four polymers produced thermally are between 35-62 °C, higher than for their corresponding copper produced counterparts, while their T_{50} and T_{max} temperatures are all within 12 °C of each other (Table 3.10).

3.3.13 Mechanical testing of C2-linked polymers prepared thermally.

The four C2 polymers prepared thermally were subjected to tensile mechanical testing. The results are a plotted average of 6 tests per polymer (Fig. 3.24). As expected, those derivatives that had significant amounts of oleate derived chains showed low tensile strength and high elongation at break; P^T(C2-AzDOA) **3.43** = 1 MPa to break, P^T(C2-AzDRSA) **3.45** = 2.5 MPa to break, while those with significant linoleic chains (and consequently cross-linking possibilities) showed tensile strengths 10-15 times stronger, P^T(C2-AzDSBA) **3.46** = 8.4 MPa, P^T(C2-AzDL) **3.44** = 15.3 MPa to break. The tensile strength parallels the azide functionality per monomer.

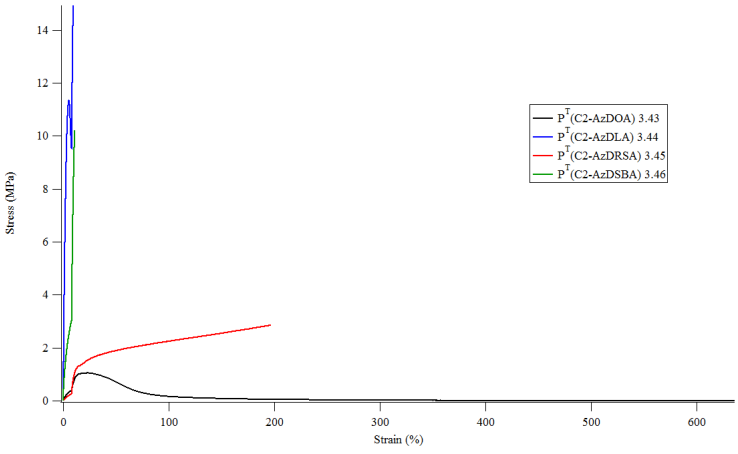


Figure 3.24: Stress strain curves for C2 thermally derived polymers.

Another characteristic of having less azide functionality is an increase in elongation at break. This is due to less cross-linking and therefore the polymer formed is more linear. As a result the polymer stretches more than a more cross-linked polymer before breaking. The Young's modulus is a measure of the elasticity of a polymer. Having a low tensile stress and a high elongation causes the polymer to have a low Young's modulus whereas having a high tensile stress and a low elongation causes higher Young's moduli (Table 3.11).

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa)[a]
P^T(C2-AzDOA) **3.43**	0.9 (±0.2)	492 (±311)	5.4 (±1.4)
P^T(C2-AzDLA) **3.44**	15.3 (±4.4)	10 (±1)	367.3 (±47)
P^T(C2-AzDRSA) **3.45**	2.6 (±0.3)	398 (±25)	4.0 (±0.3)
P^T(C2-AzDSBA) **3.46**	8.4 (±3.8)	10 (±1)	56.4 (±17)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 3.11: Mechanical testing results of C2 thermally derived polymers.

The results shows P^T(C2-AzDOA) **3.43** and P^T(C2-AzDRSA) **3.45** have low Young's moduli whereas P^T(C2-AzDLA) **3.44** and P^T(C2-AzDSBA) **3.46** have high Young's moduli indicating that the oleic and rapeseed oil derived polymers are more elastic than the linoleic and soybean oil derivatives. This is to be expected based upon the both the levels of cross-linking (azide number) and their observed T_g values. Both P^T(C2-AzDOA) **3.43** and P^T(C2-AzDRSA) **3.45** were tested above their T_g (thus in the elastic region), while P^T(C2-AzDLA) **3.44** and P^T(C2-AzDSBA) **3.46** were tested in the glassy region. However, the tensile strength and T_g values of the polymers, C2-AzDRSA **3.45** and C2-AzDSBA **3.46**, are higher than those prepared by Shah *et al*. from similar vegetable oils (Rapeseed *P^T(C2-AzRSA)* ***3.43*** *= 2.6 MPa, vs 0.9 MPa and T_g =15 ºC vs -5 ºC),* and soybean (*P^T(C2-AzSBA)* ***3.44*** *=*

8.4 MPa, vs 1.3 MPa and T_g =33 ºC vs 10 ºC). This supports the original hypothesis that increasing the hydrogen bonding potential (due to the presence of the amide functional groups) will increase the tensile strength, however further monomer modifications are required if an increase in the elasticity of polymers with higher azide functionality is desired.

3.4 Increasing the chain length of the monomers.

In order to increase the elasticity of our materials attention next turned to the effect of the linker between the two fatty acid components. The second series used a C4 linker derived from diaminobutane as the amide linker while the third series used a C6 linker derived hexamethylene diamine (Fig. 3.25). It was expected that increasing the linker would decrease the T_g and increase the elongation at break of the corresponding materials within the C2, C4, C6 linked series.

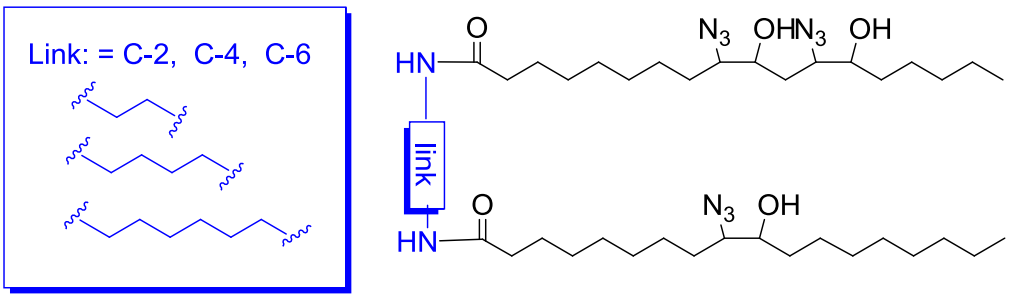


Figure 3.25: Azidated vegetable oil derived diamides with varying linkers.

3.4.1 Synthesis of C4 and C6-series of monomers

The same synthetic procedures used to make the C2 series were employed to prepare the C4 and C6 series but substituting ethylenediamine for diaminobutane or hexamethylene diamine. The four renewable feedstocks, oleic acid, linoleic acid, rapeseed oil and soybean oil were used for each series giving 8 monomers in total for the two series; C4-AzDOA **3.63**, C4-AzDLA **3.64**, C4-AzDRSA **3.65**, C4-AzDSBA **3.66**, C6-AzDOA **3.67**, C6-AzDLA **3.68**, C6-AzDRSA **3.69**, and C6-AzDSBA **3.70**. 400 MHz ^{1}H NMR shows subtle differences between C2-AzDOA **3.22**, C4-AzDOA **3.63** and C6-AzDOA **3.67** series (Fig. 3.26).

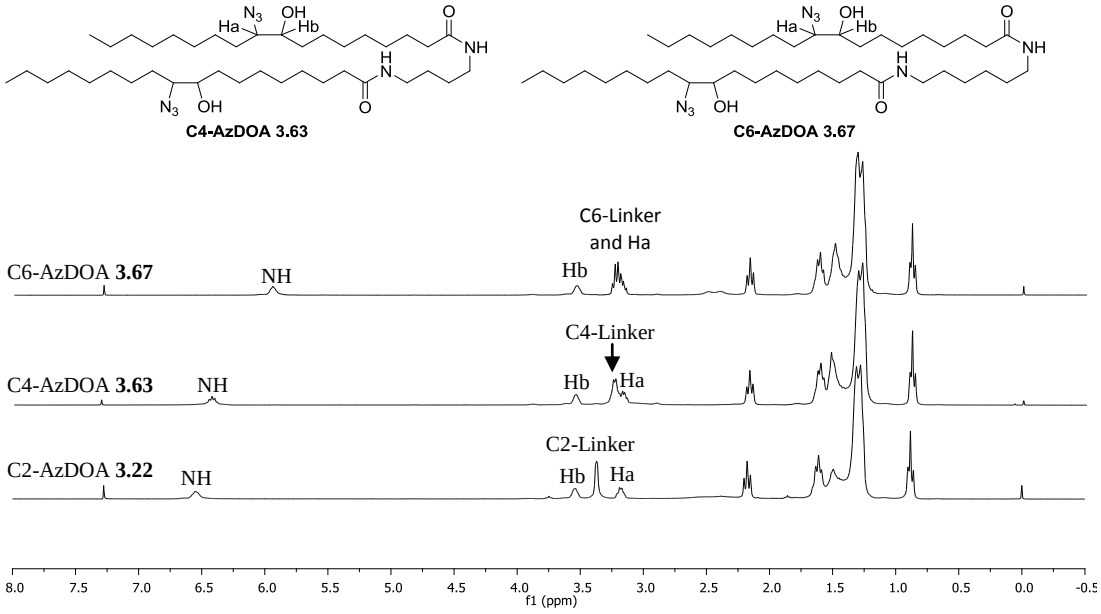


Figure 3.26: 400 MHz ^{1}H NMR comparing C2-AzDOA 3.22, C4-AzDOA 3.63 and C6-AzDOA 3.67.

Mass spectrometry (Fig 3.27a-d) of the C4 monomers shows dioleamides at $[M+Na]^{+}$ 757.5, and interestingly in the C4-AzDOA monomer a small amount of epoxide side chain accompanying an azide chain at $[M+Na]^{+}$ 714.5. Monomers with linoleic acid present show mass ion peaks at $[M+Na]^{+}$ 814.5 and $[M+Na]^{+}$ 871.5 for fully azido ring opened (C18:1, C18:2) and (2 x C18:2) side chains. Again in

soybean oil there is evidence of a mass ion peak for fully azido ring opened (2 x C17:1) side chains at $[M+Na]^+$ 729.5.

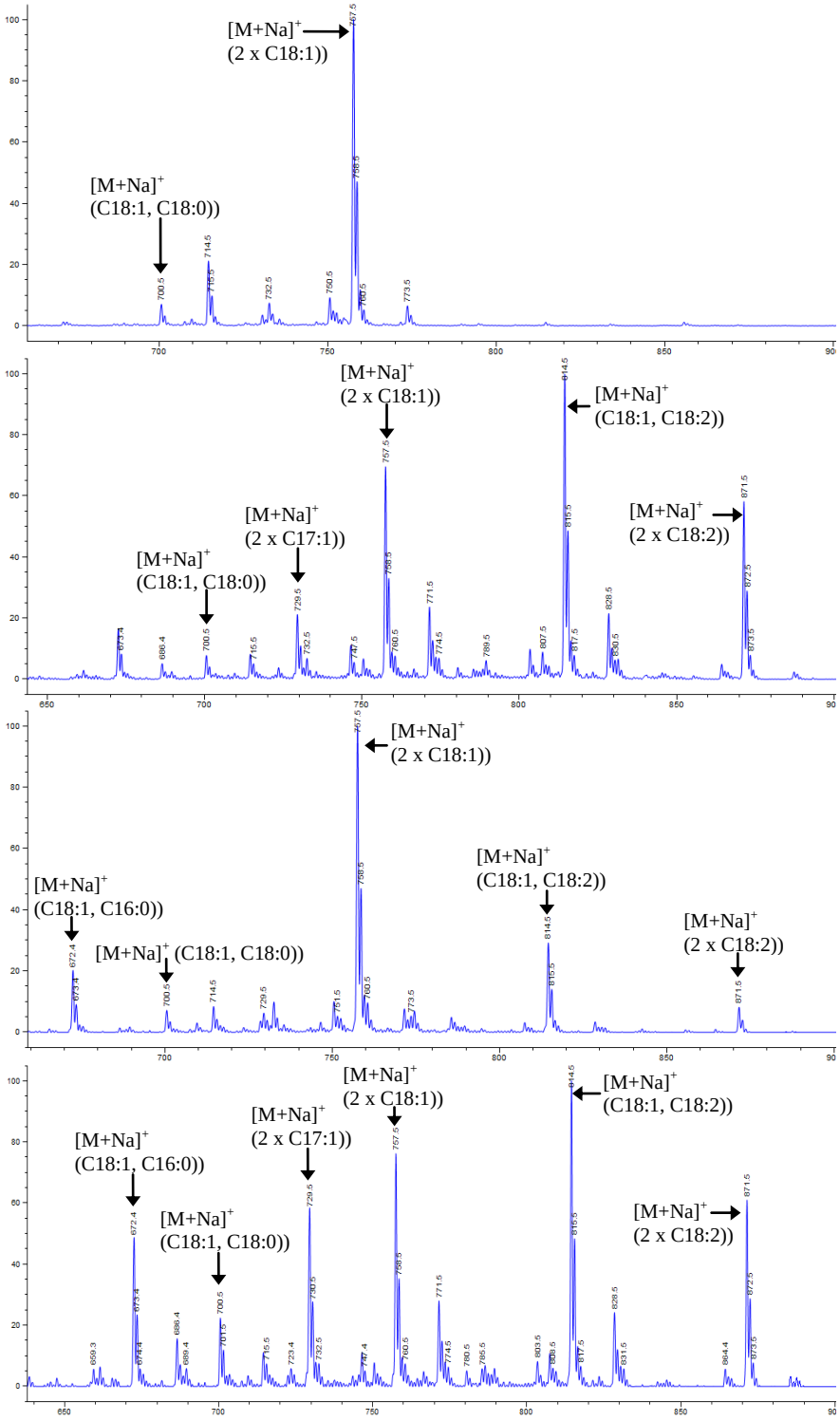


Figure 3.27: Mass spectra of (a) C4-AzDOA 3.63, (b) C4-AzDLA 3.64, (c) C4-AzDRSA 3.65, (d) C4-AzDSBA 3.66

Mass spectrometry (Fig 3.28a-b, 3.29a-b) of the C6 monomers shows dioleamides at $[M+Na]^+$ 785.5, and interestingly in the C6-AzDOA monomer a small amount of epoxide side chain accompanying an azide chain at $[M+Na]^+$ 742.5 and a smaller percentage of azido (C18:1, C18:0) side chain at $[M+Na]^+$ 728.5. Monomers with linoleic acid present show mass ion peaks at $[M+Na]^+$ 842.5 and $[M+Na]^+$ 899.5 for fully azido ring opened (C18:1, C18:2) and (2 x C18:2) side chains. Again in soybean oil there is evidence of a mass ion peak for fully azido ring opened (2 x C17:1) side chains at $[M+Na]^+$ 757.5. C6-AzDSBA also shows a mass ion peak at $[M+Na]^+$ 700.5 for diamide consisting of fully azido ring opened oleic acid and palmitic acid (C18:1, C16:0) showing the variety of diamides possible within the monomers when using triglycerides as a cheaper non-purified fatty acid sources.

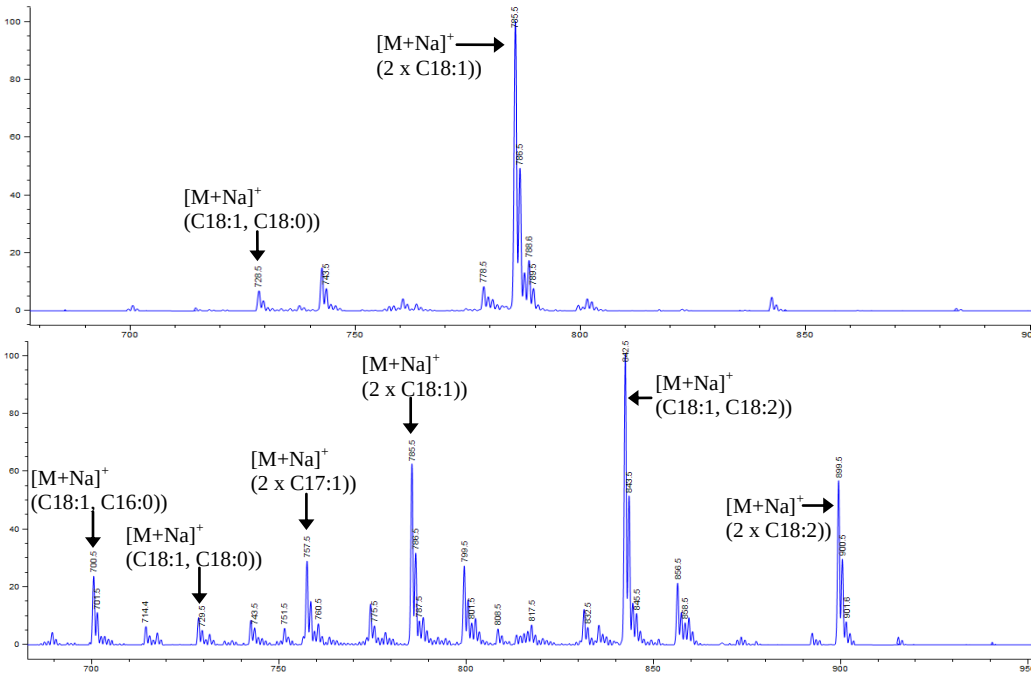


Figure 3.28: Mass spectra of (a) C6-AzDOA 3.67 and (b) C6-AzDLA 3.68.

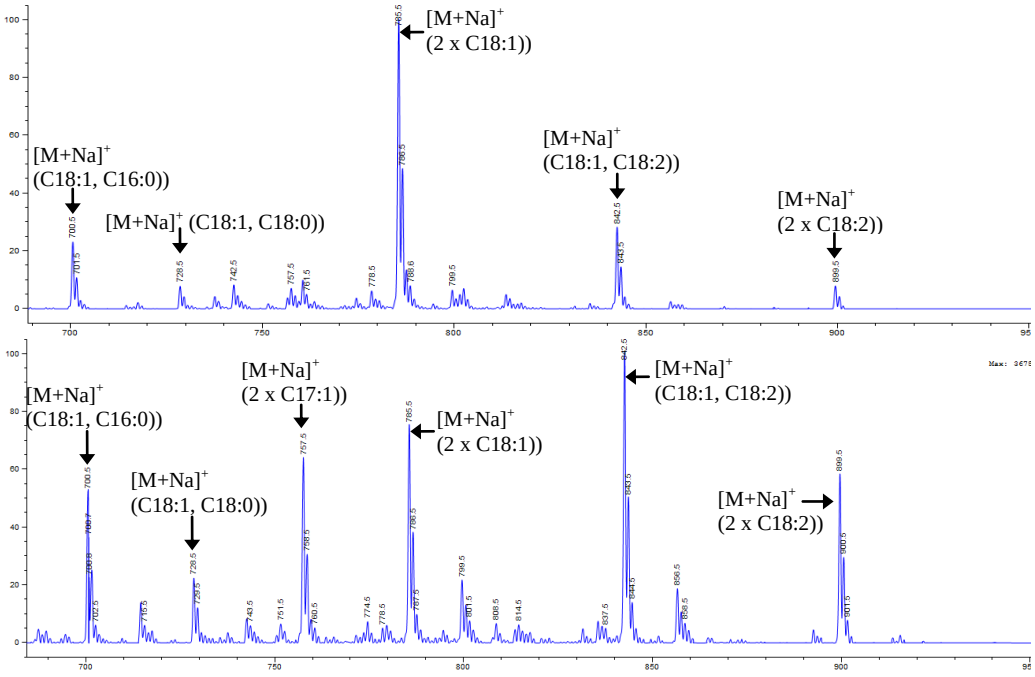


Figure 3.29: Mass spectra of (a) C6-AzDRSA 3.69 and (b) C6-AzSBA 3.70.

3.4.2 Thermal analysis of C4- and C6- derived monomers 3.63-3.70

The thermal properties of all twelve monomers are shown below (Table 3.12).

Monomer	TGA (°C)[a]			DSC (°C)[a]		N_f[b]
	$T_{10\%}$	$T_{50\%}$	T_{max}	T_g	MPt	
C2-AzDOA **3.22**	244	429	499	-21	79	1.7
C2-AzDLA **3.25**	231	402	495	-5	78	2.3
C2-AzDRSA **3.39**	236	421	500	-8	78	1.6
C2-AzDSBA **3.40**	231	413	491	-9	78	2.2
C4-AzDOA **3.63**	249	442	493	-18	79	1.6
C4-AzDLA **3.64**	228	434	505	-11	74	2.6
C4-AzDRSA **3.65**	238	439	512	-8	73	1.7
C4-AzDSBA **3.66**	230	432	501	-9	79	2.3
C6-AzDOA **3.67**	244	445	483	-14	74	1.6
C6-AzDLA **3.68**	219	430	488	-10	74	2.5
C6-AzDRSA **3.69**	240	443	491	-14	73	1.8
C6-AzDSBA **3.70**	232	439	495	-9	75	2.3

[a] DSC and TGA values measured using 10 °C /min. [b] Number of the azide groups (Nf) per triglyceride was calculated using the equation: Nf = (Mn × nitrogen content)/(molecular mass of the azide group×100).

Table 3.12: Thermal data and azide functionality level for all twelve monomers.

Thermally, all three series show the characteristic decomposition at 220 - 250 °C for the decomposition of the azide groups and all show melting points around 75 - 80 °C. In all three series the oleic acid derived monomers exhibit the lowest T_g and there is a gradual increase in T_g by 3-4 °C between the series C2-AzDOA **3.22** < C4-AzDOA **3.63** < C6-AzDOA **3.67** (Fig. 3.30). This suggests that inter chain H-bonding of the amide groups becomes more important as the tether is lengthened for this series. However, there is much less change for the other monomers containing significant amounts of linoleamide side-chains, which hints that H-bonding through the hydroxyl groups is more important. Azide functionality was calculated using the same equation as before (equation 3.1) and showed the amount of azide remained constant between the series.

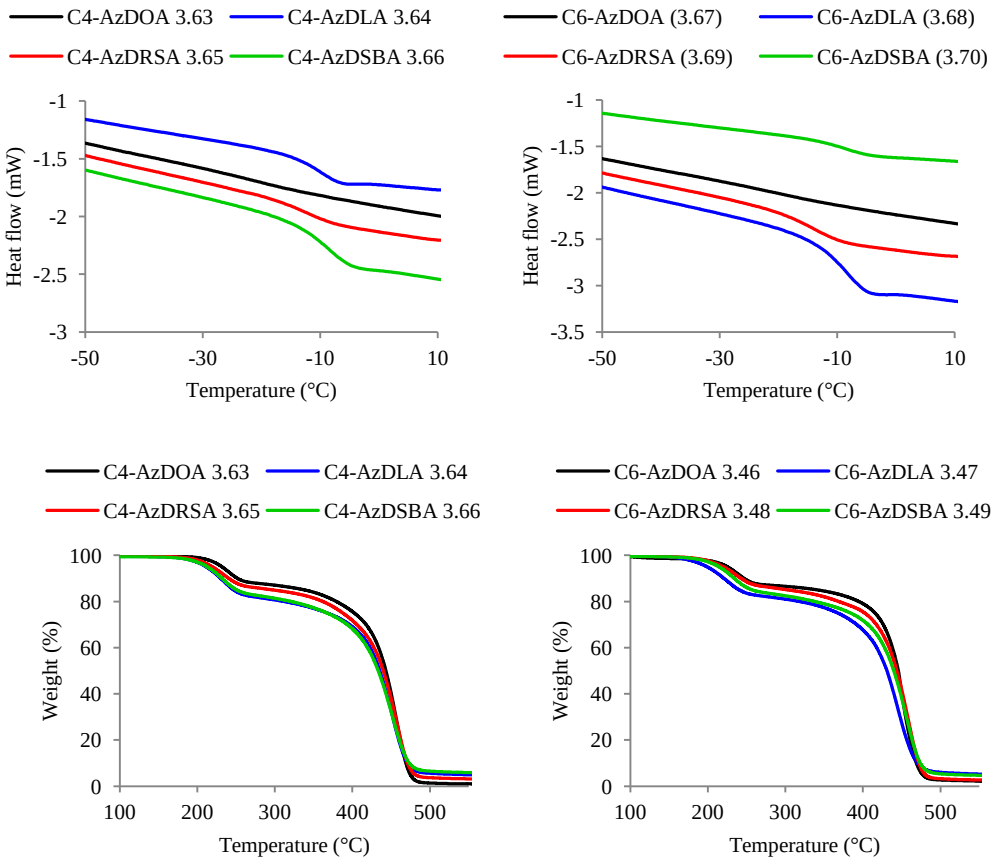


Figure 3.30: DSC and TGA of C4- and C6- monomers.

3.4.3 Polymerisation of C4- and C6- monomers *via* copper catalysis.

The C4 and C6 monomers were polymerised using the copper catalyst method used for the C2 series. Increasing the linking length of the monomer had no effect on the polymerisation rate, with the reactions forming gels in 30 mins, the P_{gel} values are the same as those calculated for the C2 series as the azide value is the same showing 87 and 91 % conversion to form gels. As for the P^{Cu}(C2-AzDOA) **3.31**, the P^{Cu}(C4-AzDOA) **3.71** and P^{Cu}(C6-AzDOA) **3.75** oleic acid derived polymers dissolved in organic solvents and therefore could be analysed by 400 MHz ^{1}H NMR, which as before showed the presence of only one regioisomer (Fig 3.31)

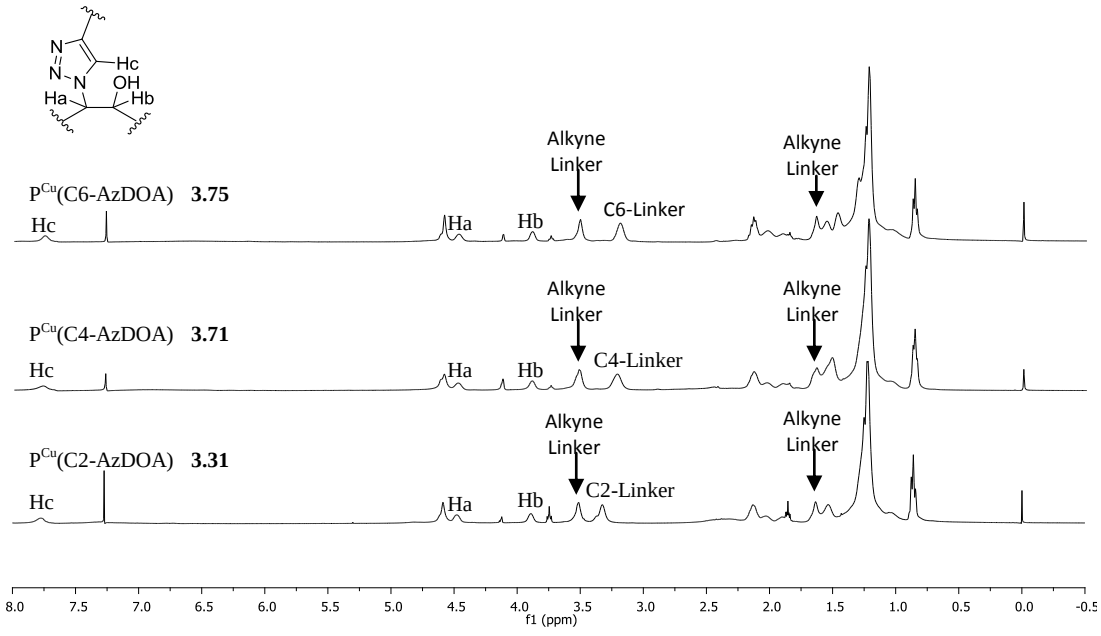


Figure 3.31: 400 MHz ^{1}H NMR comparing P^{Cu}(C2-AzDOA) 3.31, P^{Cu}(C2-AzDOA) 3.71 and P^{Cu}(C2-AzDOA) 3.75.

3.4.4 Thermal analysis of C4- and C6- derived polymers 3.71-3.78,

The data from DSC and TGA (Fig. 3.32) has been tabulated (Table 3.13).

Polymer	TGA (°C)			DSC (°C)
	T_{10}	T_{50}	T_{max}	T_g
P^{Cu}(C2-AzDOA) **3.31**	271	396	481	-13
P^{Cu}(C2-AzDLA) **3.32**	301	396	483	23
P^{Cu}(C2-AzDRSA) **3.41**	311	400	485	-2
P^{Cu}(C2-AzDSBA) **3.42**	309	396	486	25
P^{Cu}(C4-AzDOA) **3.71**	315	404	483	-7
P^{Cu}(C4-AzDLA) **3.72**	300	406	483	22
P^{Cu}(C4-AzDRSA) **3.73**	325	415	483	9
P^{Cu}(C4-AzDSBA) **3.74**	304	406	485	23
P^{Cu}(C6-AzDOA) **3.75**	328	423	488	2
P^{Cu}(C6-AzDLA) **3.76**	312	412	487	16
P^{Cu}(C6-AzDRSA) **3.77**	328	425	486	6
P^{Cu}(C6-AzDSBA) **3.78**	317	417	483	20

[a] DSC and TGA values measured using 10 °C /min.

Table 3.13: Thermal data for all polymers prepared by copper catalysis.

Two comments can be made from the data. The polymers containing more oleic acid derivatives, namely P^{Cu}(AzDOA) and P^{Cu}(AzDRSA), have lower T_g's than for those with high linoleic levels P^{Cu}(AzDLA) and P^{Cu}(AzDRSA) in all the three C2, C4 and C6 series. This is expected for reasons already highlighted previously. However, there are less obvious trends within each oil feedstock as you traverse the C2, C4 to C6 linker series. For the linoleic derived materials, namely the P^{Cu}(C2-AzDLA) **3.32**, P^{Cu}(C4-AzDLA) **3.72** and P^{Cu}(C6-AzDLA) **3.76** and P^{Cu}(AzDSBA) series the T_g decreases with an increase in linker length as expected due to decreasing cross-linking density. But for the feedstocks containing higher levels of oleic acid, namely P^{Cu}(AzDOA) and P^{Cu}(AzDRSA) there is an increase in T_g for the presumably more flexible C4 and C6 series than the less flexible C2 series. Indeed, the P^{Cu}(C4-AzDOA) **3.71** and P^{Cu}(C4-AzDRSA) **3.73** have increased by 6 °C and 8 °C respectively compared to their C2 derivatives. The reason for the increase in

these series is unclear but could be due to the amount of copper complexed to the polymer chains. Marti *et al*. carried out studies on the effect of complexation of Cu(II) salts to amides with increasing distance between the two amide chelating groups.[204] Their results show that increasing distances from C2 to C6 increased the number of available copper complexes from 1 to 3 in basic conditions; therefore materials with lower numbers of free hydroxyl groups (oleate derived materials) potentially have more of a tendency for the copper to complex to the C4 and C6 diamide functionality than the C2 series.

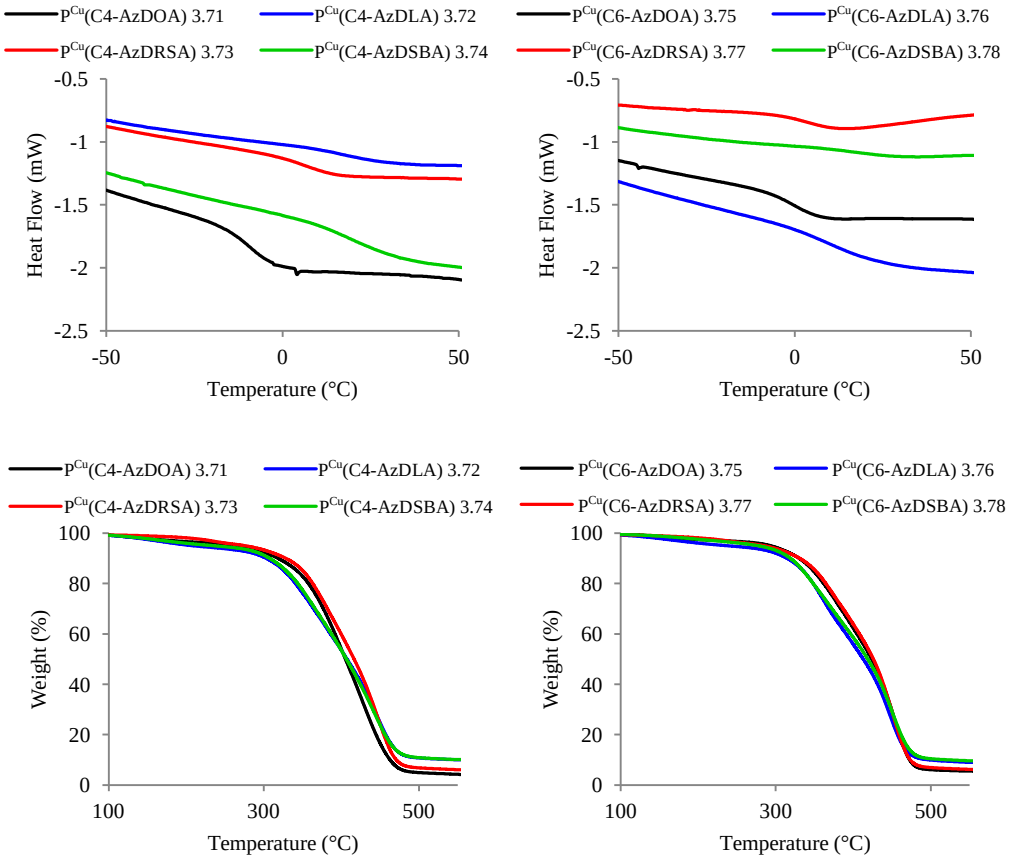


Figure 3.32: DSC and TGA of C4- and C6- polymers by copper catalysis.

TGA analysis shows there are a broad range of degradation temperatures which is characteristic of copper catalysed reactions as seen earlier in the C2 series. There is a

general increase in initial thermal stability as the linker chain length increases for the oleic AzDOA and rapeseed oils AzDRSA series however for the more cross-linked linoleic AzDLA and soybean AzDSBA series, the initial stability is lower and there is little difference between the C2 and C4 series.

3.4.5 Polymerisation of C4 and C6 monomers *via* a thermally.

To be able to mechanically test the C4 and C6 series of polymers and determine what affect the increased chain length had on their mechanical properties, the 8 monomers were also polymerised thermally. This would also allow for any inconsistencies in properties due to metal residues trapped within the polymer network to be eliminated. As before the P^T(C4-AzDOA) **3.79** and P^T(C6-ADOA) **3.83** oleic acid derived series were soluble in organic solvents and 400 MHz ^{1}H NMR analysis indicated that mixtures of 1,4- and 1,5-substituted triazoles were formed (Fig. 3.33).

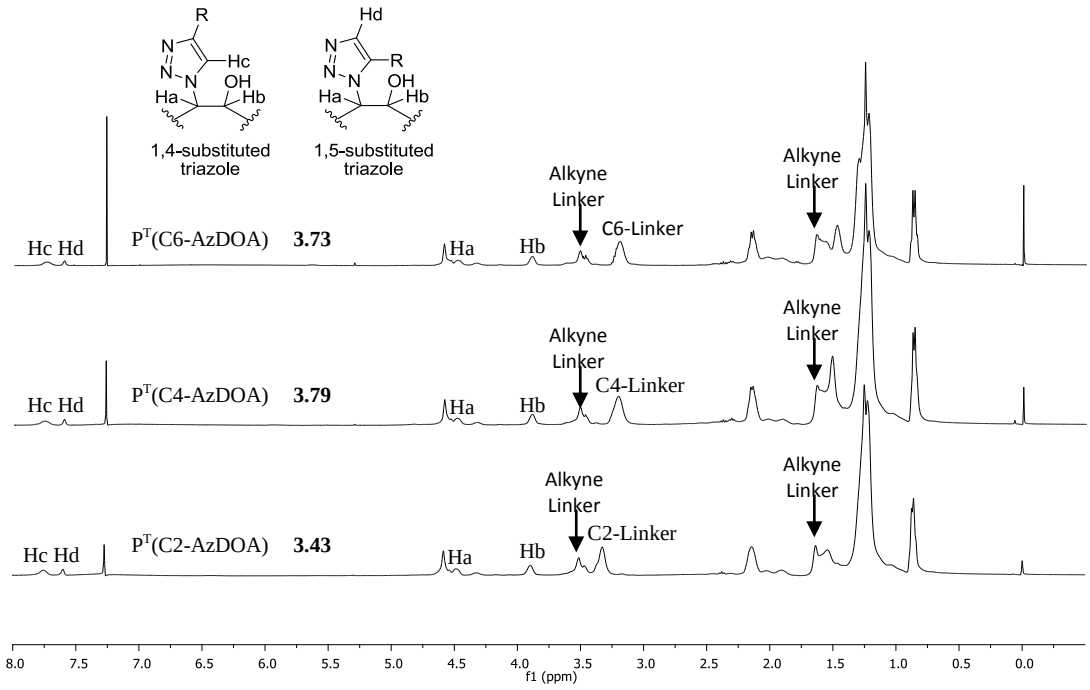


Figure 3.33: 400MHz ^{1}H NMR of P^T(C2-AzDOA), P^T(C4-AzDOA) and P^T(C6-AzDOA).

3.4.6 Thermal analysis of C4- and C6- derived polymers 3.79-3.86.

Entry	TGA (°C)			DSC (°C)
	T_{10}	T_{50}	T_{max}	T_g
P^T(C2-AzDOA) **3.43**	333	393	478	0
P^T(C2-AzDLA) **3.44**	342	396	480	35
P^T(C2-AzDRSA) **3.45**	346	388	481	15
P^T(C2-AzDSBA) **3.46**	341	400	490	33
P^T(C4-AzDOA) **3.79**	333	409	490	-4
P^T(C4-AzDLA) **3.80**	321	415	482	23
P^T(C4-AzDRSA) **3.81**	327	402	487	12
P^T(C4-AzDSBA) **3.82**	324	400	475	22
P^T(C6-AzDOA) **3.83**	341	422	481	-5
P^T(C6-AzDLA) **3.84**	338	413	483	15
P^T(C6-AzDRSA) **3.85**	227	425	479	-4
P^T(C6-AzDSBA) **3.86**	307	419	482	17

[a] DSC and TGA values measured using 10 °C /min.

Table 3.14: Thermal data for all polymers prepared thermally.

In contrast to the copper catalysis data, each series shows a lowering of the T_g from C2 through to C4 and then to the C6 series as expected (oleic $T_{g\ C2\rightarrow C4\rightarrow C6}$ = 0 °C > -4 °C > -5 °C, linoleic $T_{g\ C2\rightarrow C4\rightarrow C6}$ = 35 °C > 23 °C > 15 °C, rapeseed $T_{g\ C2\rightarrow C4\rightarrow C6}$ = 15 °C > 12 °C > -4 °C, soybean $T_{g\ C2\rightarrow C4\rightarrow C6}$ = 33 °C > 22 °C > 17 °C) (Fig. 3.34, Table 3.14). This provides more evidence that the unusual trend in the P^{Cu}(AzDOA) series, (see section 3.4.4) was due to complexed copper residues within the polymer framework. It is noteworthy that the P^T(C6-AzDRSA) polymer has a lower T_g than expected (T_g = -4 °C). This is presumably due to the polymerisation not proceeding to completion, and unreacted monomer can be detected from the TGA data, (Fig. 3.28) which shows a mass drop (12 %) characteristic of azide decomposition at 200 °C).

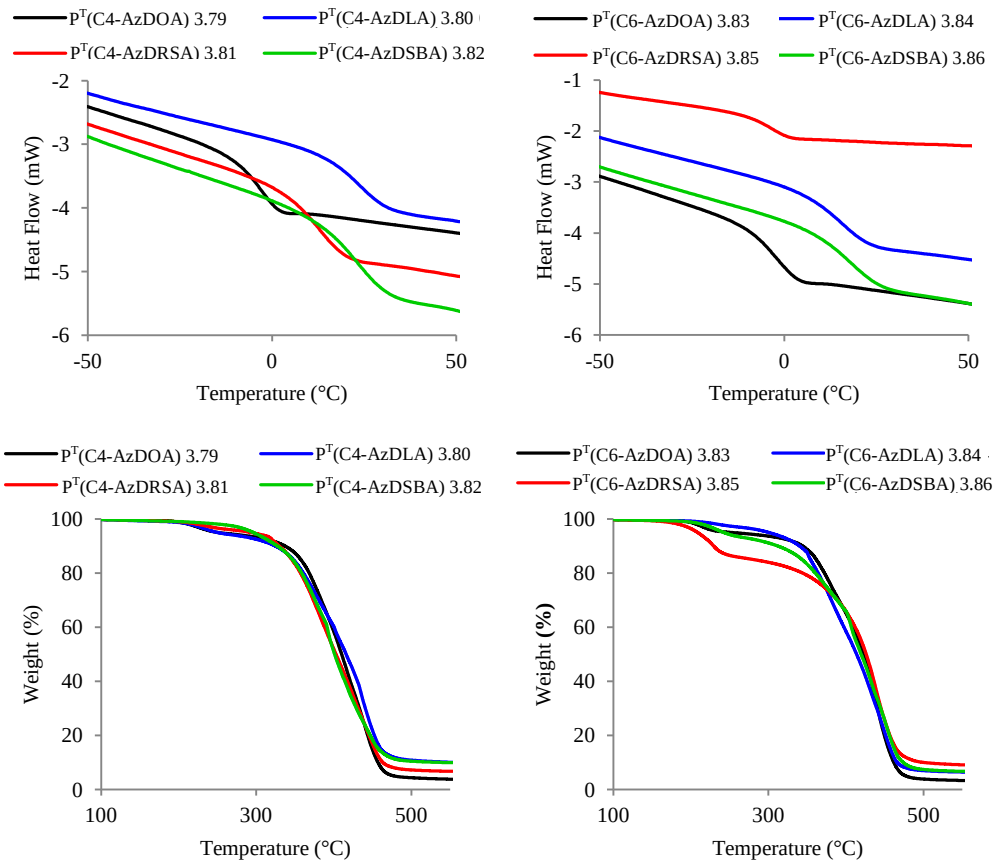


Figure 3.34: DSC and TGA of C4- and C6- thermal polymers.

The thermally produced C2, C4 and C6 polymers in each oil series show a narrower degradation region and greater thermal stability than those from the same monomers produced *via* the copper mediated process. This follows the trend seen by Shah *et al.*[138] and is due to the encapsulation of copper lowering the thermal stability for polymers produced in the catalysed process. This is best visualised in the P(AzDLA) series (Fig. 3.35). The T_{10} values are all within 20 °C of each other except for P^T(C6-AzDRSA) **3.85** and P^T(C6-AzDSBA) **3.86** which contain unreacted monomer encapsulated within the polymer.

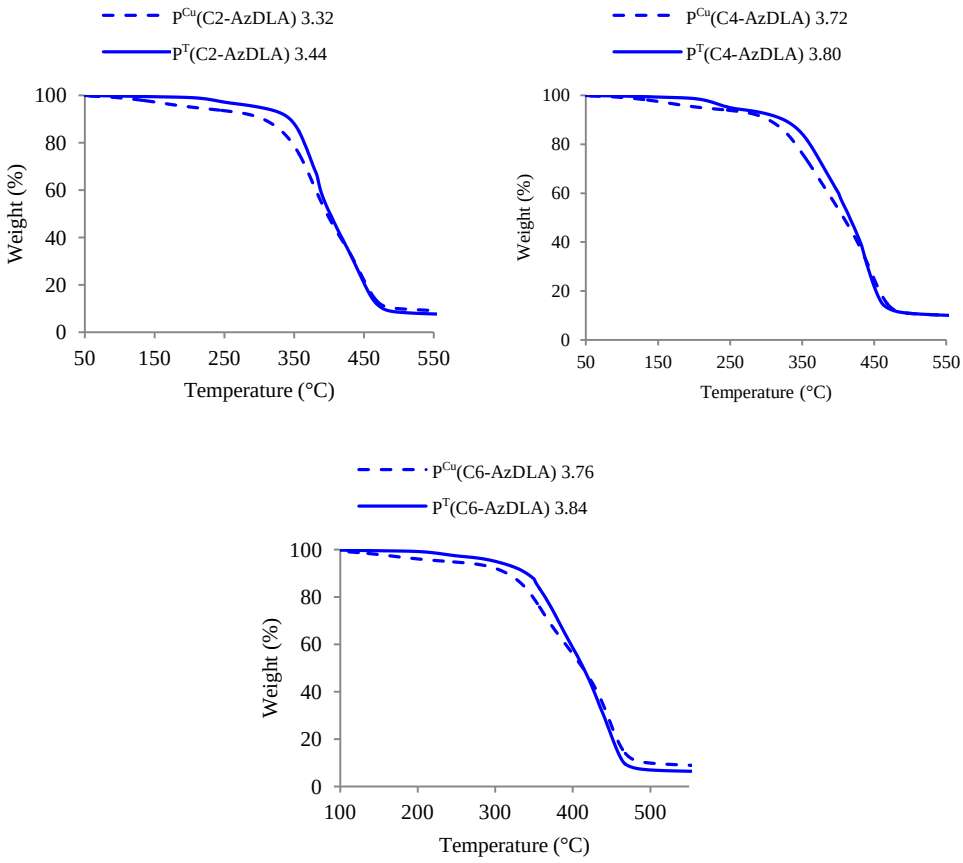


Figure 3.35: Comparison TGA's for C2, C4 and C6-P(AzDLA) derived thermally and by copper catalysis.

3.4.7 Mechanical testing of C4- and C6-linked polymers prepared thermally.

As before the mechanical testing was undertaken on all 8 of the thermally produced C4- and C6-tethered polymers and data compared to that obtained for the C2- series (Table 3.16). In all three linker length series, materials containing higher percentages of linoleic derived chains AzDLA and AzDSBA have greater tensile strengths and lower elongation at break than for those derived primarily from oleate side chains. Stress strain curves for the C4 and C6 series of polymers can be seen in appendix 2. The same trend in tensile strength seen for the C2 polymers can be seen in the C4 and C6 series. The main points from this data are; the increase in elongation due to

the increase in linker length (P^T(*C2-AzDLA*) ***3.44*** *= 10 %*, P^T*(C4-AzDLA)* ***3.80*** *= 44 % and* P^T*(C6-AzDLA)* ***3.84*** *= 137 %* and decrease in tensile strength (P^T(*C2-AzDLA)* ***3.44*** *= 15.3 MPa,* P^T*(C4-AzDLA)* ***3.80*** *= 11.7 MPa and* P^T*(C6-AzDLA)* ***3.84*** *= 3.6 MPa*) caused by the increased distance between cross-linking (Fig. 3.36). The oleic, rapeseed oil and soybean oil derived polymer stress strain curves can be seen in appendix 2.

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa)[a]
P^T(C2-AzDOA) **3.43**	0.9 (±0.2)	493 (±311)	5.4 (±1.4)
P^T(C2-AzDLA) **3.44**	15.3 (±4.4)	10 (±1)	367.3 (±47.0)
P^T(C2-AzDRSA) **3.45**	2.6 (±0.3)	398 (±25)	4.0 (±0.3)
P^T(C2-AzDSBA) **3.46**	8.4 (±3.8)	10 (±1)	56.4 (±17.0)
P^T(C4-AzDOA) **3.79**	0.2 (±0.1)	1738 (±814)	1.3 (±1.0)
P^T(C4-AzDLA) **3.80**	11.7 (±3.6)	44 (±13)	73.3 (±22.4)
P^T(C4-AzDRSA) **3.81**	3.1 (±0.8)	219 (±11)	2.1 (±0.3)
P^T(C4-AzDSBA) **3.82**	14.6 (±2.6)	38 (±15)	69.8 (±22.7)
P^T(C6-AzDOA) **3.83**	0.4 (±0.1)	1728 (±130)	1.6 (±1.0)
P^T(C6-AzDLA) **3.84**	3.6 (±0.8)	137 (±39)	2.9 (±1.4)
P^T(C6-AzDRSA) **3.85**	1.0 (±0.1)	254 (±73)	8.7 (±3)
P^T(C6-AzDSBA) **3.86**	6.0 (±0.7)	129 (±68)	7.9 (±1.4)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 3.15: Mechanical testing results of C2 and C4 thermal polymers.

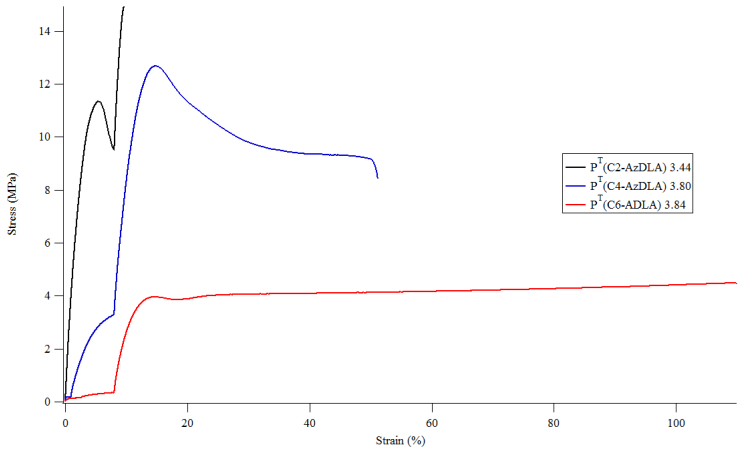


Figure 3.36: Mechanical properties of P^T(C2-AzDLA), P^T(C2-AzDLA) and P^T(C2-AzDLA).

All samples show necking where the sample deforms without breaking however P^T(C2-AzDLA) **3.44** shows strain hardening where the deformation hardens relative to its cross sectional area and the sample increases in strength again before fracture.

3.5 Summary and Conclusion

A range of fatty diamides can be synthesised with varying thermal and mechanical properties. The tensile strength of the amide polymers, P^T(C2-AzDOA) **3.43**, P^T(C2-AzDLA) **3.44**, P^T(C2-AzDRSA) **3.45** and P^T(C2-AzDSBA) **3.46**, are higher than the polymers synthesised by Shah *et al*. (*P^T(C2-AzDLA)* ***3.44*** *= 15.3 MPa, linseed* ***3.19*** *= 3.39 MPa*). The elasticity of the polymers with lower azide functionality increased considerably when compared with those synthesised by Shah *et al.* (*P^T(C2-AzDOA)* ***3.43*** *= 493 %, castor* ***3.16*** *= 54 %*), however the elasticity of those with increased azide functionality has decreased (*P^T(C2-AzDLA)* ***3.44*** *= 10 %, linseed* ***3.19*** *= 61 %*). Thermal stability of the amide polymers also decreased slightly when compared to the polymers synthesised by Shah *et al.*, T_{50} P^T(C2-AzDLA) **3.44** = 396 °C, linseed **3.16** = 402 °C, ΔT_{50} = -6 °C, however the T_g values have increased greatly (*P^T(C2-AzDLA)* ***3.44*** *= 35 °C, linseed* ***3.16*** *= 16 °C, ΔT_g = 19 °C*). Increasing the linker length from C2 to C4 and C6 increased the elongation of the polymers (*P^T(C2-AzDLA) (**3.44**) = 10 %, P^T(C4-AzDLA)* ***3.80*** *= 44 % and P^T(C6-AzDLA)* ***3.84*** *= 137 %*) and decreased the tensile strength (*P^T(C2-AzDLA)* ***3.44*** *= 15.3 MPa, P^T(C4-AzDLA)* ***3.80*** *= 11.7 MPa and P^T(C6-AzDLA)* ***3.84*** *= 3.6 MPa*) due to increased distance between cross-linking. Polymers with higher azide functionality and C6 linker had higher tensile strengths than the highest synthesised by Shah *et al.* (*P^T(C6-AzDLA)* ***3.84*** *= 3.6*

MPa, linseed ***3.18*** *= 3.4 MPa*) and also demonstrated higher elongation (P^T*(C6-AzDLA)* ***3.84*** *= 137 %, linseed* ***3.18*** *= 61 %)* demonstrating increasing the hydrogen bonding within the polymer network will increase elongation whilst retaining tensile strength.

3.6 Future Work

It has been established from the work carried out in this chapter that azide functionality, hydrogen bonding and diamide length are key features that affect the polymer thermal and mechanical properties. Increasing the azide functionality is less desirable as high amounts of azide can cause instability in the monomer, therefore the best area to further examine this relationship is in the remainder of the monomer structure and the linker used in polymerisation.

As hydrogen bonding had such an effect on increasing polymer thermal and mechanical properties it would be interesting to see if other intermolecular interactions have a similar effect. To test this hypothesis aromatic linkers could be incorporated into the monomer, starting with aromatic difatty esters to minimise the hydrogen bonding effect seen from the diamides, subsequently increasing the amide content using 4 aminophenol and 1,4-phenylenediamine. It is envisaged that the pi stacking effect would increase the T_g and tensile strength but decrease the elasticity

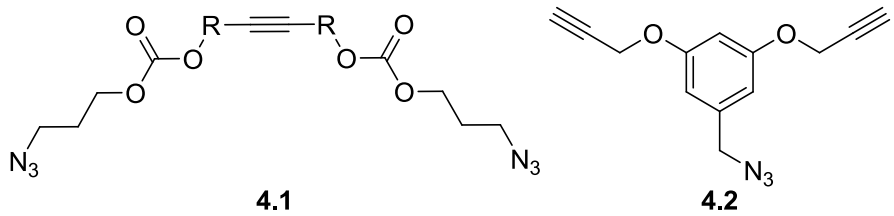
Increasing the length of the amide linker from C2 to C6 increased the elasticity of the polymers significantly whilst lowering the tensile strength significantly. C2 was found to have the higher tensile strength with minimal elongation; it is therefore possible that increasing the length of the dialkyne linker could increase the elasticity

of the polymer while maintaining the tensile strength. In order to test this hypothesis a library of increasing length dialkyne linkers should be established and polymerised with the C2 monomers to determine if increasing the distance between the polymer chains has an effect on the hydrogen bonding ability as well as increasing the polymer network. It is envisaged the increase in distance between the polymer chains would decrease the hydrogen bonding ability, whether it is substantial enough to decrease the tensile strength and T_g is to be determined.

4.0 Alkyne-Azide Click Homopolymers Derived from Renewable Oils

4.1 Introduction

Very little work has previously been done incorporating azide and alkyne functionalities within the same molecule for polymer synthesis.[133,205] In 2004, Scheel *et al.* synthesised novel hyperbranched poly(1,2,3-triazole)s derived from AB_2-Type monomers.[133] The first monomer involved two azide functionalities and one alkyne unit **4.1**, the second involved two alkyne units and one azide unit **4.2** (Fig. 4.1). Both monomers were synthesised using reactions proceeding at room temperature to minimise premature self-polymerisation. Samples were stored at -20 °C as self-polymerisation was seen in monomer samples stored above 0 °C.

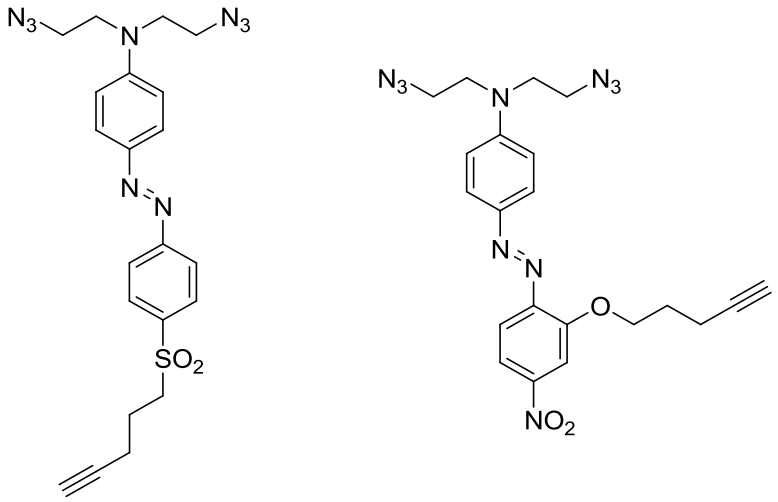


4.1 **4.2**

Figure 4.1: AB_2 monomers 4.1 and 4.2 prepared by Scheel *et al.*[133]

Polymers were synthesised from **4.1** and **4.2** either thermally or with copper-mediated cycloaddition. Thermally generated polymers showed the characteristic traces of the 1,5-disubstituted 1,2,3-triazole moiety, as seen in chapter 3, whereas those polymerised using copper catalysis showed only the 1,4-disubstituted triazole. Both monomers successfully produced hyperbranched poly(1,2,3-triazole)'s leaving either unreacted azide units, or alkyne units, which would allow further modification of the hyperbranched polymers. In 2011 Li *et al.* expanded on this approach by

synthesising end-capped hyperbranched poly(1,2,3-triazole)s.[205] The main backbone of the 2 polytriazoles was synthesised from two monomers, **4.3** and **4.4** (Fig 4.2) and each contained 2 azide functionalities and 1 alkyne unit.



4.3 **4.4**

Figure 4.2: Li *et al.* monomers 4.3 and 4.4 for polytriazole synthesis.[205]

The second unreacted azide functionality was further functionalised in the more conventional azide-alkyne click reaction with a second alkyne monomer to give a series of different end-capped hyperbranched polytriazoles with a range of solubilities and thermal and optical properties for use in non-linear optics.

4.2 Aims and objectives

Results from chapter 3 indicated that the properties of azide-alkyne click AB polymers derived from azidated fatty acid linked dimers **4.5** and dialkyne **3.26** are influenced by a) the renewable oil feedstock, b) any additional H-bonding possibilities within the monomers and linkers and c), the length of linker between the H-bonding and azide functionalities, (Fig. 4.3). In general, additional H-bonding

increased tensile strength, while increasing linker size (and distance between azide functionality) decreased it.

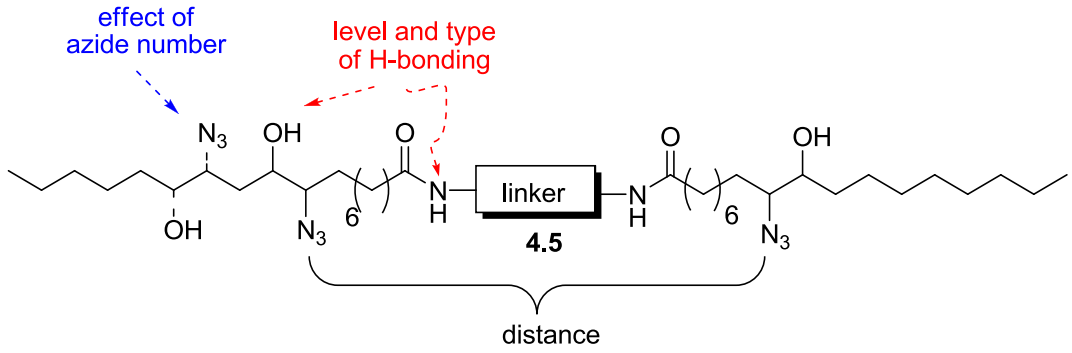


Figure 4.3: Factors effecting thermal and mechanical properties of polymers in chapter 3.

In this chapter investigations are carried out to establish whether the same effects are observed in the preparation of fatty acid derived homopolymers, Consequently, a range of monomers **4.6** derived from different fatty acids that contained BOTH azide and alkyne functionality were prepared, (Fig 4.4). By varying the linker between the two reactive functionalities one could determine the effect on the polymer properties of:

- Linker length (distance between reactive functionality).
- Type of atom X and level of H-bonding within the monomer.
- Level of azide and alkyne functionality.

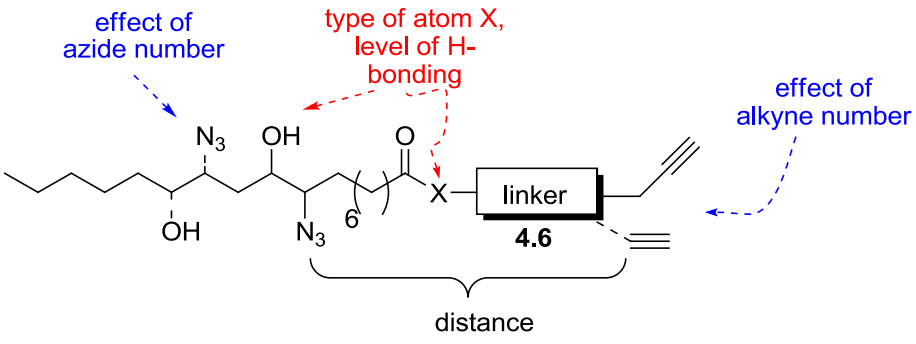


Figure 4.4: Factors probed in design of monomers for homopolymerisation.

Specifically, a range of monomers **4.7**-**4.11** derived from oleic acid, linoleic acid, hydrolysed rapeseed oil and hydrolysed soybean oil (Fig 4.5) were prepared. Comparing the properties of polymers produced from **4.7** with **4.8** would allow assessment of the effect of linker length, while comparing **4.8** with **4.9** would allow investigation into the relative effect of additional H-bonding. Comparison of **4.10** with **4.11** would allow the effect of the number of alkynes in the monomer to be investigated while comparison of oleic with linoleic derived materials within each series would allow assessment of the effect of the number of azide groups.

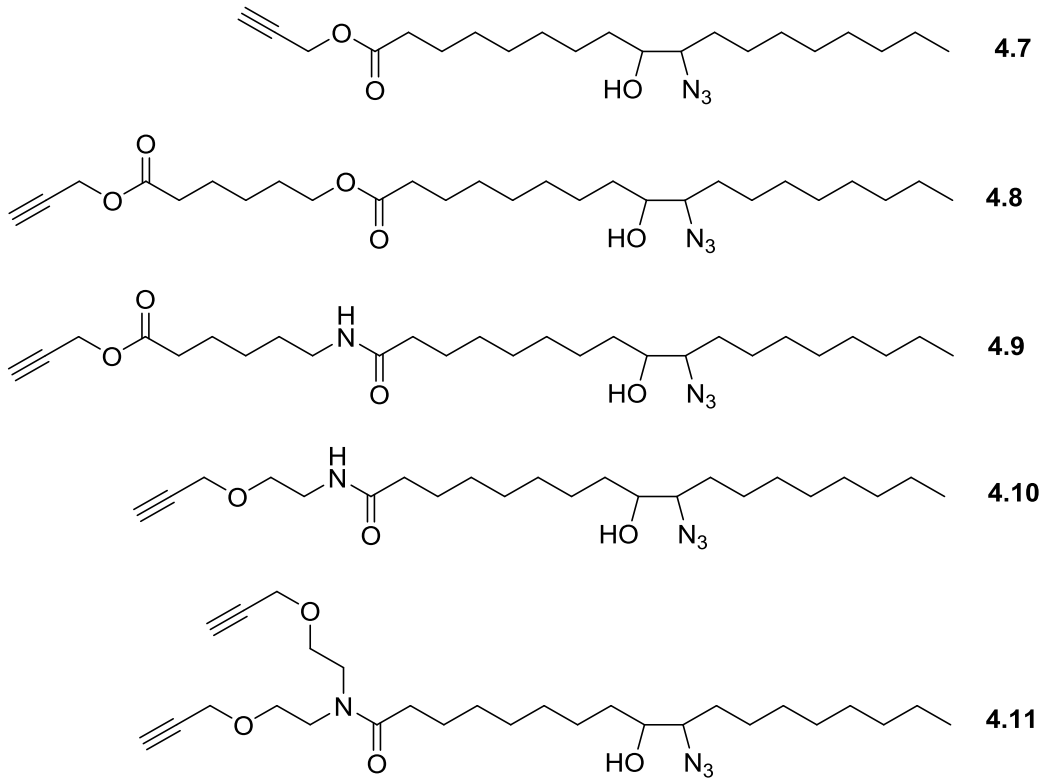


Figure 4.5: Monomers to be used in this study. Only oleic acid derived monomers shown.

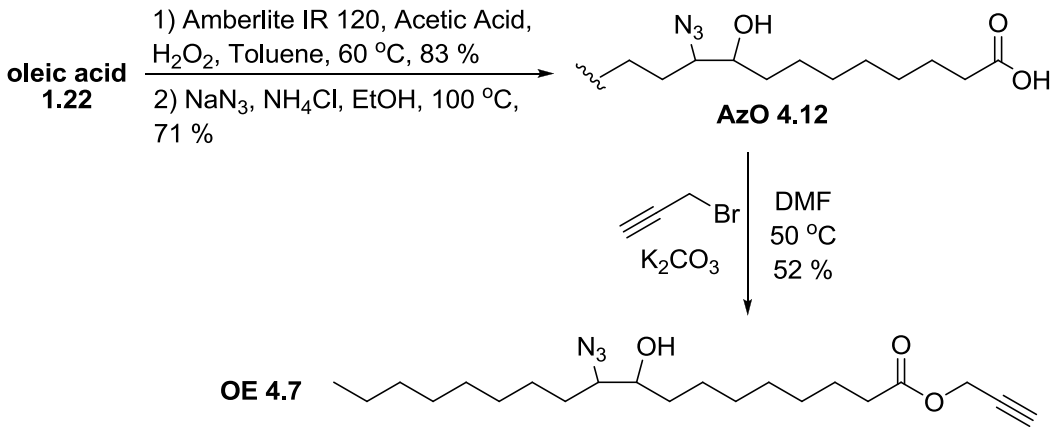
As in previous chapters a bespoke nomenclature was employed to describe the monomers and polymers. Monomers: (**4.7** = Oleic ester **OE 4.7**, linoleic ester **LE**

4.7, rapeseed ester, **RSE 4.7**, soybean ester **SBE 4.7**); (**4.8** = Extended oleic ester **ExOE 4.8**, **ExLE 4.8**, **ExRSE 4.8**, **ExSBE 4.8**); (**4.9** = Extended oleic amide **ExOA 4.9**, **ExLA 4.9**, **ExRSA 4.9**, **ExSBA 4.9**); (**4.10** = Ethanolamine derived oleic amide **EtOA 4.10**, **EtLA 4.10**, **EtRSA 4.10**, **EtSBA 4.10**); (**4.11** = DiEthanolamine derived oleic amide **DEtOA 4.11**, **DEtLA 4.11**, **DEtRSA 4.11**, **DEtSBA 4.11**). Polymers of these monomers will be recorded by adding the prefix 'P' in front of the appropriate abbreviation.

4.3 Propargyl Derived Fatty Ester Based Homopolymers P4.7

4.3.1 Synthesis of OE 4.7, LE 4.7, RSE 4.7 and SBE 4.7.

In order to establish the effect of increasing the distance between the reacting azide and alkyne functionality in the homopolymers, the propargyl linked materials **4.7** were first prepared, (Scheme 4.1). This gave a benchmark from which to compare. Two approaches were available for the synthesis of the monomers **4.7**; the first approach (method 1) incorporates the alkyne first and then the azide *via* an epoxide ring opening, the second approach (method 2) reverses these operations by introducing the azide first followed by the alkyne. Preliminary studies on both routes showed a small amount of polymerisation occurred during the azide ring-opening of the epoxide in method 1. As a result, method 2 was chosen as the optimum route and a representative approach from oleic acid is described, (Scheme 4.1). Epoxidation was achieved using the Amberlite® method, described in chapter 2, and afforded the desired epoxidised fatty acids in 83 – 87 % yields.



Scheme 4.1: Synthesis of propargyl ester monomers.

Azidation was achieved by the sodium azide, ammonium chloride in ethanol and water (5:1) method described in chapter 3, however less equivalents of sodium azide were required therefore making the procedure slightly less hazardous. This gave the respective azidated fatty acids **4.12** in 71 – 83 % yields. Addition of the alkyne group was successfully achieved using potassium carbonate and propargyl bromide in DMF at 50 °C and afforded the desired monomers OE **4.7**, LE **4.7**, RSE **4.7** and SBE **4.7** in 52 – 69 % yields after purification.

The 400 MHz ^{1}H NMR spectra of epoxidised oleic acid, azidated derivative **4.12** and monomer OE **4.7**, (Fig 4.6), shows the characteristic proton shift for the protons of the epoxide (2.92 ppm) have disappeared upon reaction with sodium azide to give **4.12** (Ha = 3.19 ppm azide, Hb = 3.55 ppm OH). The protons of the alkyne Hd and CH_2 of the propargyl group Hc can be observed at 2.47 ppm and 4.68 ppm respectively in final monomer **OE 4.7**.

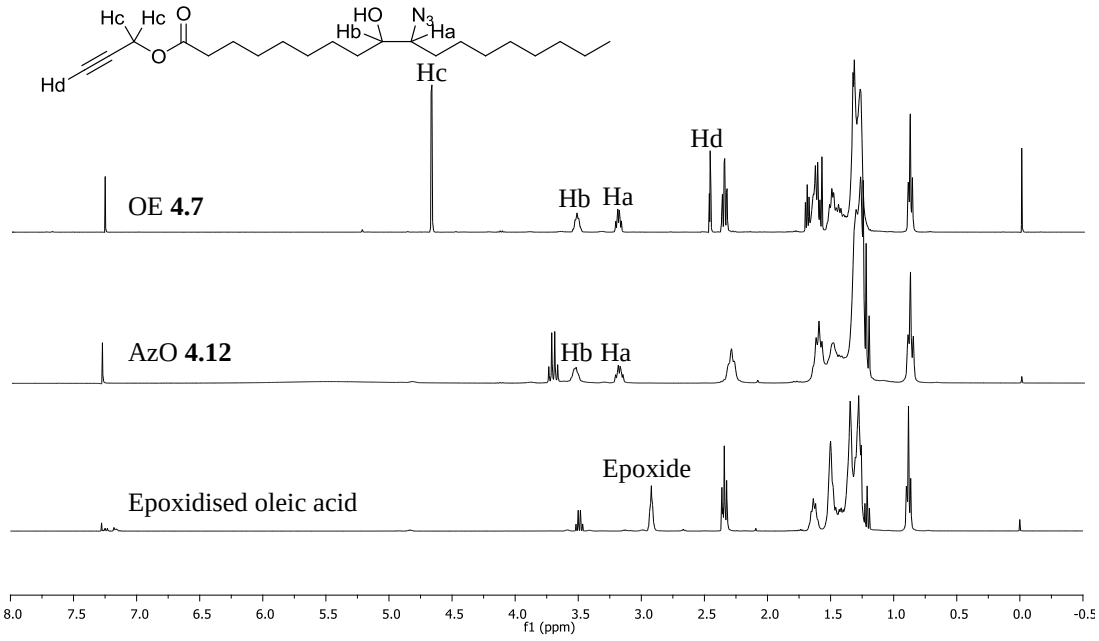


Figure 4.6: 400 MHz ^{1}H NMR spectrum showing epoxidised oleic acid, 4.12 and OE 4.7.

Mass spectrometry of the oleate monomer (Fig 4.7) shows the mass ion peak at $[M+Na]^+$ 402.3 and a small percentage of epoxy propynyl oleate at $[M+Na]^+$ 359.2. The linoleic and triglyceride based monomers (Fig 4.8a-c) show the oleate monomer at $[M+Na]^+$ 402.3 and the linoleate monomer at $[M+Na]^+$ 459.3 and a small amount for 1 azido 1 epoxy linoleate side chain at $[M+Na]^+$ 416.2, interestingly no peak can be seen for epoxy oleate chains.

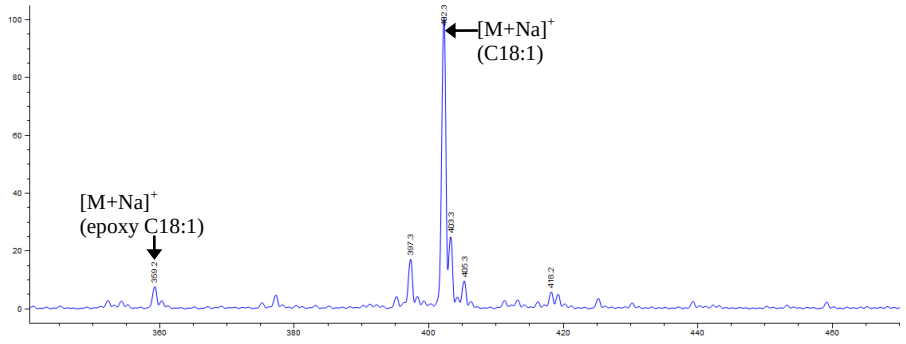


Figure 4.7: Mass spectrum of OE 4.7 monomer.

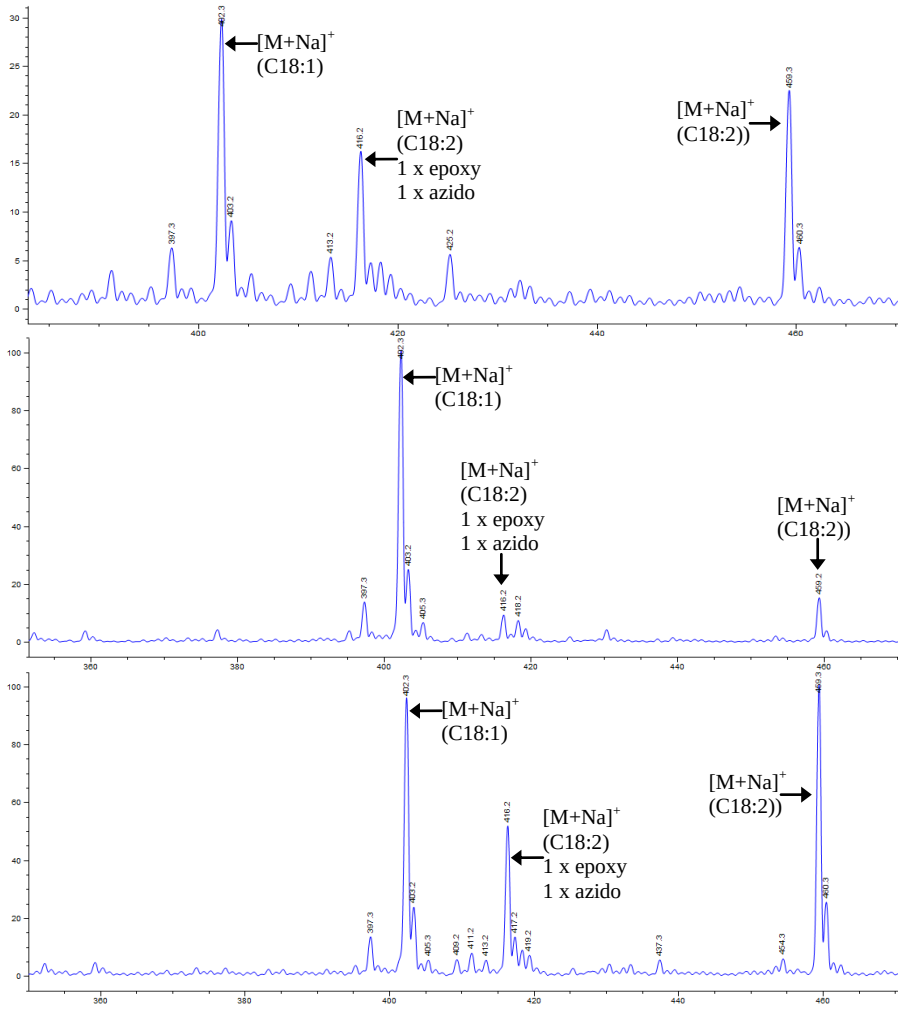


Figure 4.8: Mass spectra of LE 4.7, RSE 4.7 and SBE 4.7 monomers.

4.3.2 Thermal analysis of OE 4.7, LE 4.7, RSE 4.7 and SBE 4.7 monomers.

Thermal analysis was carried out on OE **4.7**, LE **4.7**, RSE **4.7** and SBE **4.7**. DSC shows an endotherm around 165 °C showing the curing point of the monomers (appendix 3).

	Oleic acid[a]	Linoleic acid[a]	Rapeseed Oil[a]	Soybean Oil[a]
Palmitic Acid	0.0 %	0.0 %	5.2 %	12.2 %
Stearic Acid	3.0 %	0.0 %	1.5 %	5.0 %
Oleic Acid	97.0 %	40.0 %	60.5 %	24.8 %
Linoleic Acid	0.0 %	60.0 %	31.1 %	57.7 %

[a] Fatty acid composition determined by FAME analysis

Table 4.1: Fatty Acid composition of fatty acids, rapeseed oil and soybean oil.

Glass transition temperatures (T_g) show similar trends to those observed in chapter 3 for similar reasons. Thus, OE **4.7** has the lowest T_g = *-61 °C* and the two materials with significant linoleic acid components have the highest, (Table 4.1, 4.2) DSC traces can be seen in appendix 3. Upon heating, all monomers show 2 step degradations with the second degradation occurring around 420 °C and above 50 % weight loss (Fig. 4.9). Unlike for the monomers described in chapter 3 there is no initial weight loss caused by azide decomposition presumably due to homopolymerisation taking place during the heating cycle.

Monomer	DSC (°C)[a]		TGA (°C)[a]			Azide Functionality[b]
	T_g	Cure Point	T_{10}	T_{50}	T_{max}	
OE **4.7**	-61	161	339	400	479	0.8
LE **4.7**	-42	168	352	392	483	1.1
RSE **4.7**	-48	167	325	386	484	0.9
SBE **4.7**	-27	162	319	386	485	1.1

[a] DSC and TGA values measured using 10 °C /min. [b]Number of the azide groups (Nf) per monomer was calculated using the equation: Nf = (Mn × nitrogen content)/(molecular mass of the azide group×100).

Table 4.2: Thermal data of PAzOE, PAzLE, PAzRSE and PAzSBE (4.15 – 4.18) monomers.

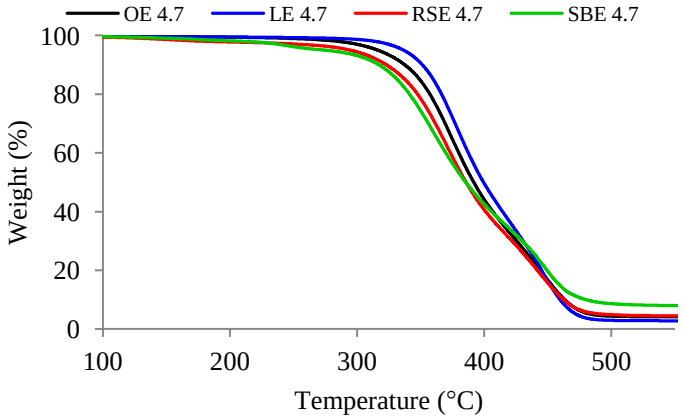
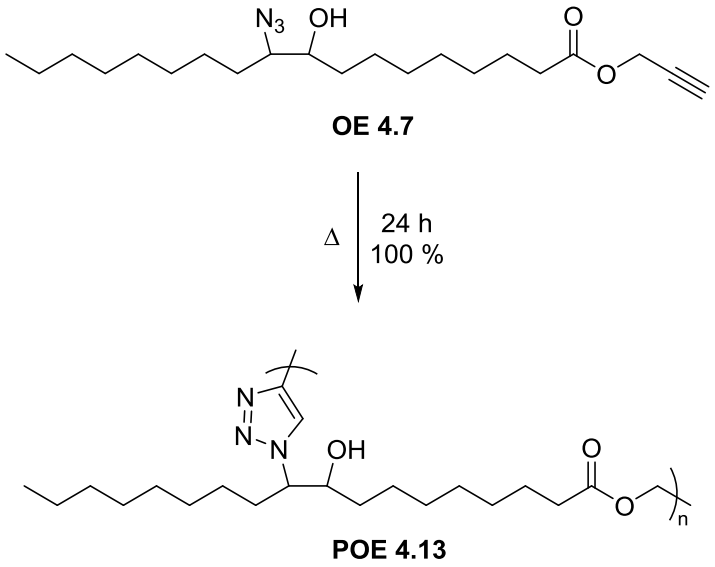


Figure 4.9: TGA of OE4.7, LE4.7, RSE4.7 and SBE4.7 monomers.

4.3.3 Homopolymerisation of OE 4.7, LE 4.7, RSE 4.7 and SBE 4.7 monomers

Polymerisations could be achieved using both the copper catalysed and thermal methods described in chapter 3. However, as previously discussed, to be able to synthesise samples suitable for mechanical testing the thermal method was employed. While the DSC of the monomers showed the maximum cure point to be around 165 °C, polymerisation was initially investigated at 100 °C using silicone moulds to prepare dog-bones for mechanical testing. The monomer was heated to 50 °C in a vacuum oven for 5 hours, to remove residual solvent and encapsulated air, followed by 24 hours at 100 °C (Scheme 4.2).



Scheme 4.2: Polymerisation of OE 4.7 to POE 4.13.

The polymers synthesised were not soluble in organic solvents therefore GPC was not possible, this is presumably due a) the degree of branching caused by the linoleic acid moiety in PLE **4.13**, RSE **4.13** and SBE **4.13** and b) the molecular weight of the oleic polymer POE **4.13** potentially being larger than the polymers seen in the

previous chapter, which were soluble in organic solvents, due to a better reactive group stoichiometric balance.

4.3.4 Thermal analysis of POE 4.13, PLE 4.13, PRSE 4.13 and PSBE 4.13.

Polymerisation of OE **4.7** gave a linear polymer POE **4.13** with the lowest T_g -7 °C, while PRSE, **4.13** gave linear polymers with a small degree of branching caused by the linoleic acid moiety present and therefore a higher T_g 1 °C. Both materials PLE **4.13** and PSBE **4.13** with larger azide numbers and higher levels of linoleic side-chains and subsequently the highest T_g's 21 °C and 22 °C respectively. As expected the glass transition temperatures (T_g) have increased significantly (Table 4.3) upon polymerisation with increase between 49 °C – 63 °C (*PRSE **4.13** ΔT_g = 49 °C, PLE **4.13** ΔT_g = 63 °C*).

Monomer/Polymer	DSC (°C)[a]	TGA (°C)[a]		
	T_g	T_{10}	T_{50}	T_{max}
OE **4.7**	-61	339	400	479
LE **4.7**	-42	352	392	483
RSE **4.7**	-48	325	386	484
SBE **4.7**	-27	319	386	485
POE **4.13**	-7	320	376	488
PLE **4.13**	21	325	390	491
PRSE **4.13**	1	323	385	488
PSBE **4.13**	22	319	387	481

[a] DSC and TGA values measured using 10 °C /min.

Table 4.3: Thermal comparison between monomers 4.7 and polymers 4.13.

TGA shows the thermal stability of the fatty acid derived polymers has decreased from the monomer stability, (Fig. 4.10). However PLE **4.13** and PSBE **4.13** show the characteristic azide drop around 220 °C caused by the unreacted azide in the

polymer.[200] This is to be expected as the azide groups were in excess over the alkyne groups 1.1:1.0 in both materials, (see Table 4.2). T_{max} for monomers **4.7** and polymers **4.13** are all within 12 °C which is expected due to the monomers **4.7** polymerising during their thermal analysis tests.

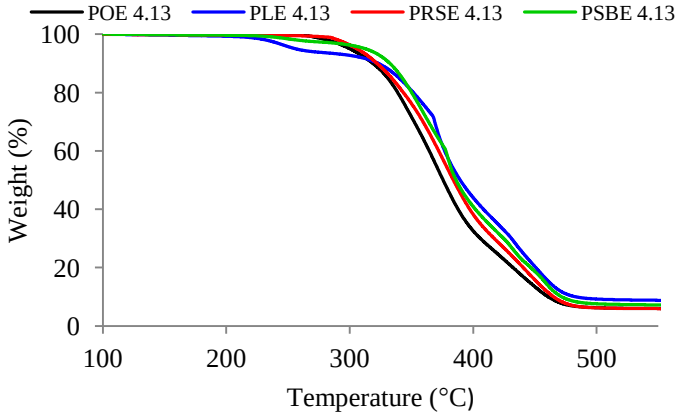


Figure 4.10: TGA of POE 4.13, PLE 4.13, PRSE 4.13 and PSBE 4.13.

4.3.5 Mechanical testing of POE 4.13, PLE 4.13, PRSE 4.13 and PSBE 4.13

Having successfully synthesised the polymers **4.13** in the desired shape, mechanical testing was undertaken to determine the physical properties in order to establish a benchmark for homopolymers (Table 4.4).

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa)[a]
POE **4.13**	0.1 (±0.02)	229 (±41)	0.1 (±0.03)
PLE **4.13**	5.1 (±0.78)	208 (±36)	2.7 (±0.04)
PRSE **4.13**	0.3 (±0.08)	658 (±36)	0.1 (±0.01)
PSBE **4.13**	0.6 (±0.13)	220 (±16)	0.3 (±0.10)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 4.4: Mechanical testing of PAzOE, PAzLE, PAzRSE and PAzSBE (4.19 – 4.22) polymers.

POE **4.13** has the lowest tensile strength as expected (UTS = 0.1 MPa) with PRSE **4.13** showing similar properties, however has a slightly higher tensile strength due to the extra branching. PLE **4.13** has the highest tensile strength due to significant branching but both PRSE **4.13** and PSBE **4.13** are considerably weaker, presumably due to lower molecular weights caused by capping of chains by saturated fatty groups. PSBE **4.13** is slightly stronger due to greater branching than in PRSE **4.13**. Figure 4.12 shows the stress strain curve of the 4 polymers **4.13**. This shows the polymers do not exceed their elastic limit, this is also further corroborated by the samples returning to their original shape post fracture (Fig. 4.11). PLE and PSBE **4.13** show a small degree of necking, which is where a material's cross-sectional area decreases by a greater proportion than the material strain hardens, followed by stabilisation (strain hardening) where the neck begins to harden allowing the material to deform in other areas.

Figure 4.11: Intact and fractured polymer PLE 4.13.

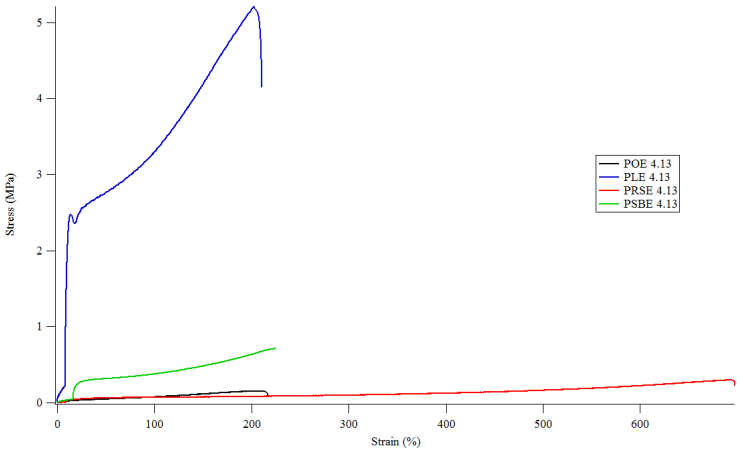
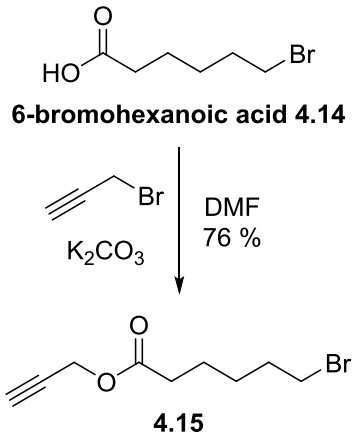


Figure 4.12: Stress strain curves of polymers 4.13.

4.4 Fatty Acid Extended Propargyl Ester Based Homopolymers

4.4.1 Synthesis of extended ester monomers 4.8.

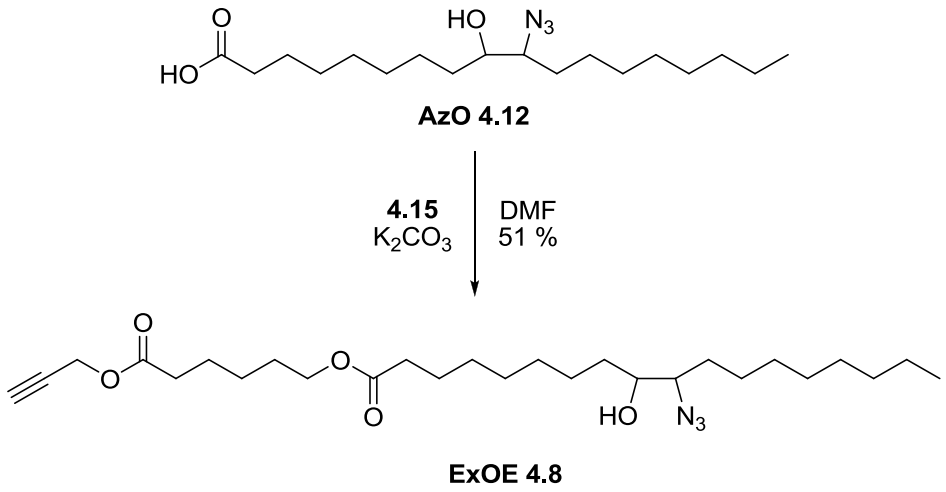
Having successfully synthesised monomers **4.7** and mechanically tested the resultant polymers **4.13** to establish a standard on which to compare any further polymers, a similar range of monomers ExOE **4.8**, ExLE **4.8**, ExRSE **4.8** and ExSBE **4.8**, with increased chain length between the alkyne and azide functionality were synthesised. This was achieved by incorporating a second ester subunit using prop-2-ynyl 6-bromohexanoate **4.15**. The subunit was synthesised from 6-bromohexanoic acid **4.14** and propargyl bromide using the same esterification procedure used to synthesise OE **4.7** from AzO **4.12**, however, to prevent the synthesis of dimers of 6-bromohexanoic acid, the propargyl bromide was added immediately after the addition of the potassium carbonate (Scheme 4.3). The reaction produced prop-2-ynyl 6-bromohexanoate **4.15** in 76 % yield after purification.



Scheme 4.3: Synthesis of prop-2-ynyl 6-bromohexanoate 4.24 subunit.

The extended series of monomers **4.8** were then synthesised from the corresponding azido fatty acids **4.12** and the prop-2-ynyl 6-bromohexanoate **4.15** subunit using the

same esterification reaction used for the previous series **4.7** (Scheme 4.4). ExOE **4.8**, ExLE **4.8**, ExRSE **4.8** and ExSBE **4.8** were synthesised in 52 – 61 % yields. ^{1}H 400 MHz NMR (Fig. 4.13) compares the two monomers OE **4.7** and ExOE **4.8**.



Scheme 4.4: Synthesis of ExOE 4.8.

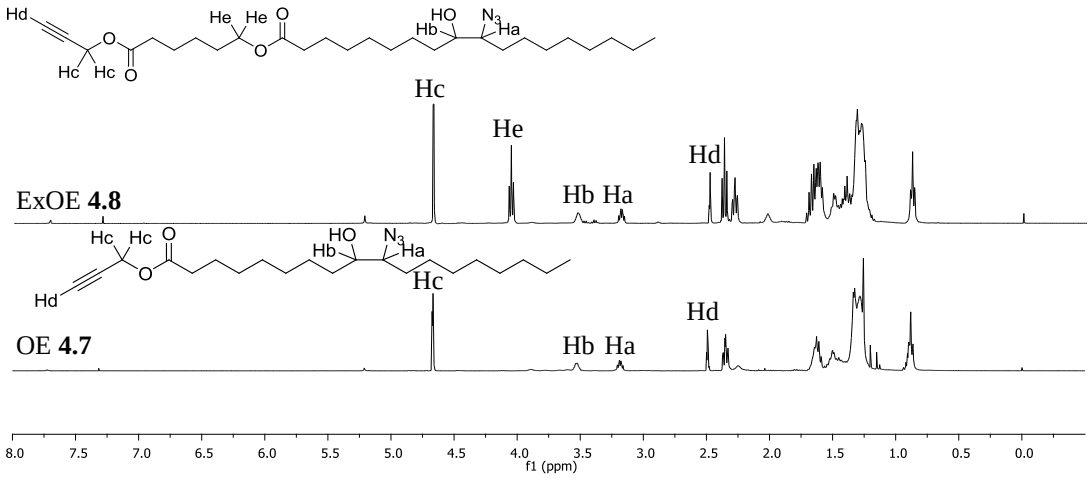


Figure 4.13: 400 MHz ^{1}H NMR spectrum of OE 4.7 and extended ExOE 4.8.

Mass spectrometry of the oleate monomer (Fig 4.14a) shows the mass ion peak at $[M+Na]^{+}$ 516.3 and a small percentage of epoxy oleate at $[M+Na]^{+}$ 473.3. The

linoleic and triglyceride based monomers (Fig 4.14b-c, Fig 4.15) show the oleate monomer at $[M+Na]^+$ 516.3 and the linoleate monomer at $[M+Na]^+$ 573.3 and a small amount for 1 azido 1 epoxy linoleate side chain at $[M+Na]^+$ 530.2, a small peak can also be seen for epoxy oleate chains at $[M+Na]^+$ 473.3 in ExLE **4.8** and ExSBE **4.8** however not in the ExRSE **4.8**.

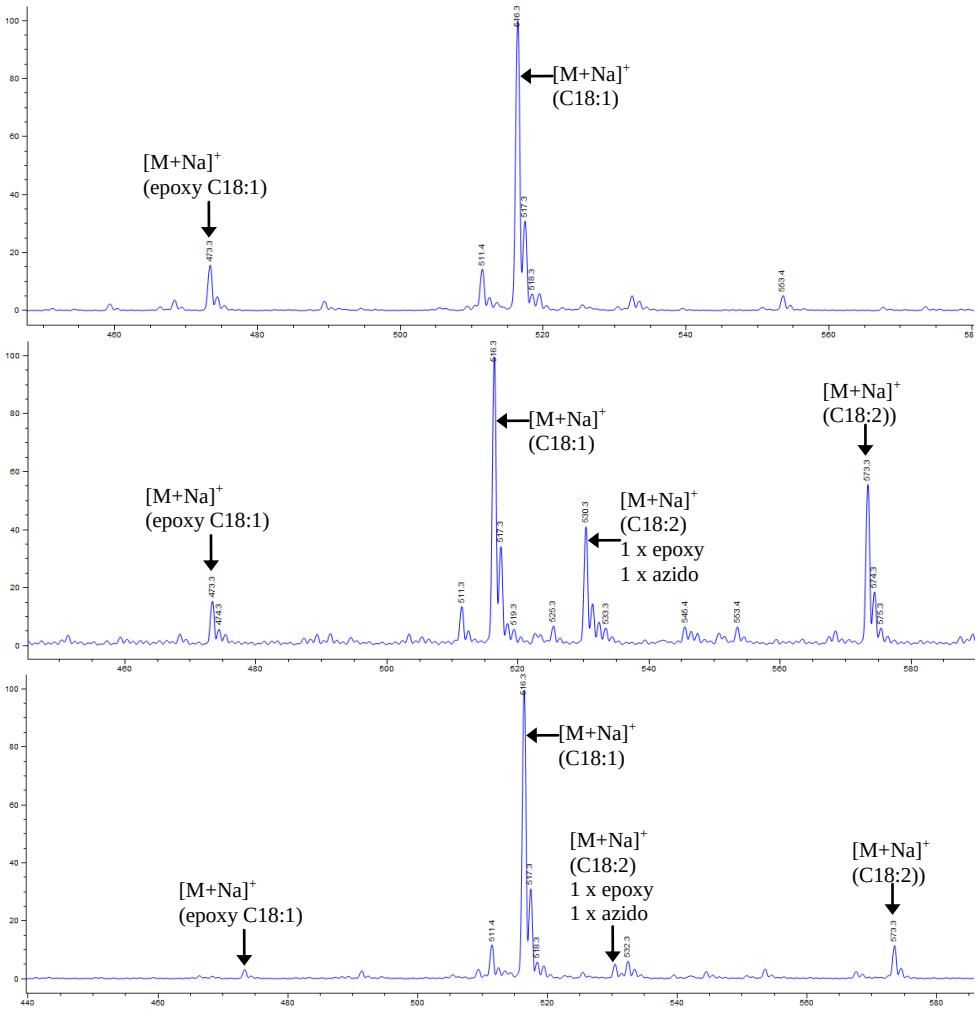


Figure 4.14: Mass spectra of ExOE 4.8, ExLE 4.8 and ExRSE 4.8 monomers.

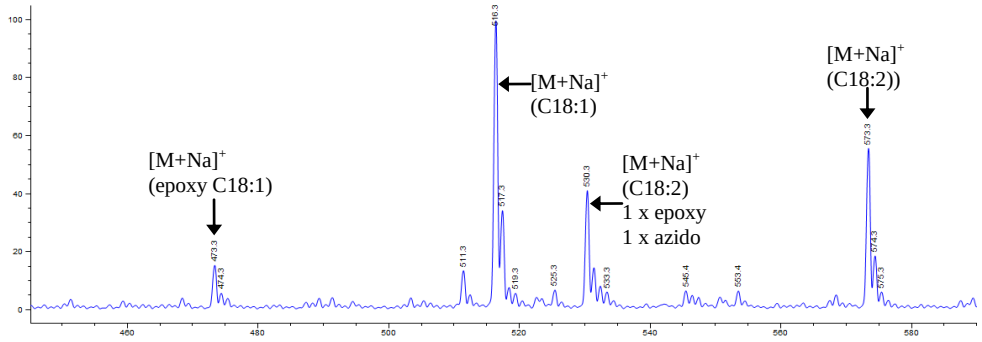


Figure 4.15: Mass spectrum of ExSBE 4.8 monomer.

4.4.2 Thermal analysis of extended monomers 4.8.

DSC (appendix 3) shows the T_g of the monomers **4.8** has decreased between 16 °C - 32 °C compared to monomers **4.7** upon incorporation of the more flexible linker as expected, (Table 4.5). DSC also shows the cure point is around 7 °C lower in the extended series **4.8** than the control series **4.7**.

Monomer	DSC (°C)[a]		TGA (°C)[a]		
	T_g	Cure Point	T_{10}	T_{50}	T_{max}
OE **4.7**	-61	161	339	400	479
LE **4.7**	-42	168	352	392	483
SE **4.7**	-48	167	325	386	484
SBE **4.7**	-27	162	319	386	485
ExOE **4.8**	-68	163	336	393	492
ExLE **4.8**	-67	160	274	371	492
ExRSE **4.8**	-64	161	332	395	500
ExSBE **4.8**	-58	155	309	392	498

[a] DSC and TGA values measured using 10 °C /min.

Table 4.5: Thermal comparison of monomers 4.7 and 4.8.

Thermal stability remains similar between the two series, the extended series however, T_{max} is 10 °C – 15 °C higher (*OE **4.7** T_{max} = 479 °C, ExOE **4.8** T_{max} = 492 °C*) due to increased molecular weight of the monomer (Fig. 4.14).

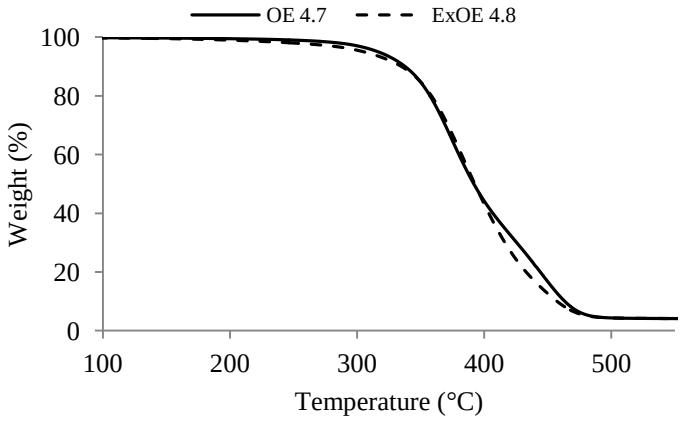


Figure 4.16: TGA of POE 4.7 and ExOE 4.8 monomers.

4.4.3 Polymerisation of extended monomers 4.8

Polymerisation was achieved using the same protocol described in section 4.3.3 to give **4.16**. Again the polymers **4.16** were not soluble in organic solvents therefore GPC data could not be obtained.

4.4.4 Thermal analysis of extended polymers 4.16

Glass transition temperatures, T_g, have again increased significantly upon polymerisation from the monomer **4.8** to the polymer **4.16** by between 50 – 57 °C (*ExRSE **4.8** T_g = -64 °C, PExRSE **4.16** T_g = -14 °C*).

Polymer	DSC (°C)[a]	TGA (°C)[a]		
	T_g	T_{10}	T_{50}	T_{max}
POE **4.13**	-7	320	376	488
PLE **4.13**	21	325	390	491
PRSE **4.13**	1	323	385	477
PSBE **4.13**	22	319	387	481
PExOE **4.16**	-38	317	377	500
PExLE **4.16**	-3	338	387	500
PExRSE **4.16**	-14	329	383	483
PExSBE **4.16**	-1	339	397	488

[a] DSC and TGA values measured using 10 °C /min.

Table 4.6: Thermal comparison of control series 4.13 and extended series 4.16.

However, the T_g of extended materials **4.16** is still lower than the control **4.13** series, by 15 – 31 °C (Table 4.6) due to the greater flexibility within the polymer chains, and this agrees with the hypothesis from chapter 3. As before, decomposition of azide groups can be seen around 230 °C for PExLE **4.8** and PExSBE **4.8**, suggesting azide terminated materials. Thermal stability of polymers **4.16** is still high, with T_{10} around 320 – 330 °C and are, generally, higher than the control series **4.13** (*PRSE **4.13** T_{10} = 323 °C, PExRSE **4.16** T_{10} = 329 °C, ΔT_{10} = 6 °C*). As expected due to the increase in chain length, T_{max} is slightly higher for the extended series **4.16** when compared to the control series **4.13** (Fig. 4.17).

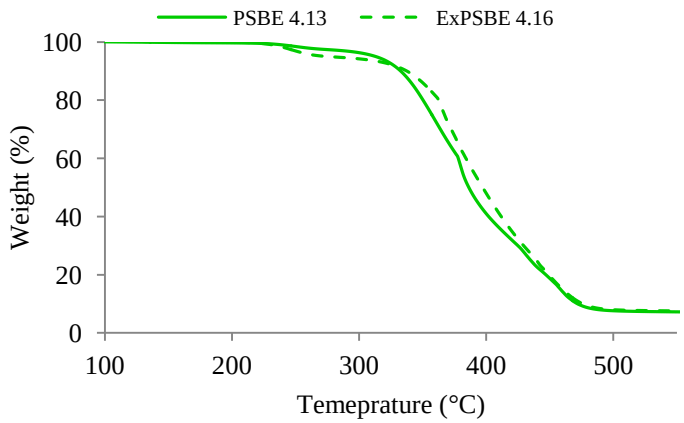


Figure 4.17: TGA comparison between PSBE 4.13 and PExSBE 4.16.

4.4.5 Mechanical testing of extended polymers 4.16.

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa)[a]
POE **4.13**	0.1 (±0.02)	229 (±41)	0.1 (±0.03)
PLE **4.13**	5.1 (±0.78)	208 (±36)	2.7 (±0.04)
PRSE **4.13**	0.3 (±0.08)	658 (±36)	0.1 (±0.01)
PSBE **4.13**	0.6 (±0.13)	230 (±16)	0.3 (±0.10)
PExOE **4.16**	-	-	-
PExLE **4.16**	0.6 (±0.02)	176 (±2)	0.5 (±0.12)
PExRSE **4.16**	0.3 (±0.05)	454 (±54)	0.1 (±0.04)
PExSBE **4.16**	0.5 (±0.06)	292 (±35)	0.2 (±0.04)

Where: UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. [a] Values in brackets are error analysis based on standard deviation.

Table 4.7: Mechanical data comparison between the control 4.13 and extended series 4.16.

Unfortunately, PExOE **4.16** was too soft at room temperature to be mechanically tested. As expected, Young's modulus, which is a measure of the elasticity of a polymer, for the extended series has decreased, this shows increasing the chain length of the polymer has increased the elongation but decreased the strength (Table 4.7). A stress strain curve comparison between the two series, PSBE **4.13** and PExSBE **4.16** can be seen below (Fig. 4.18). All the stress strain curves for the extended propargyl polymers can be found in appendix 3.

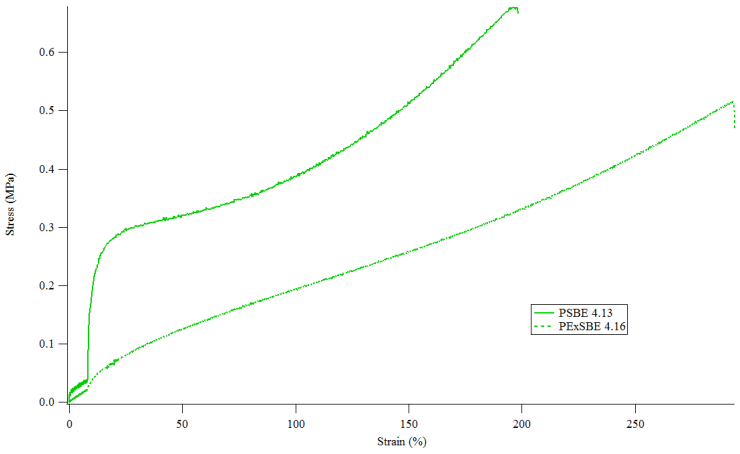
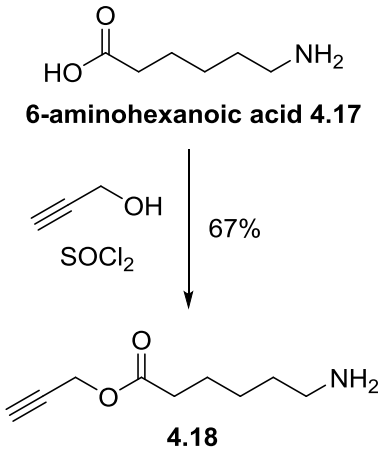


Figure 4.18: PSBE 4.13 and PExSBE 4.16 stress-strain comparison.

4.5 Fatty Acid Extended Propargyl Amide Based Homopolymers

4.5.1 Synthesis of extended amide monomers 4.9

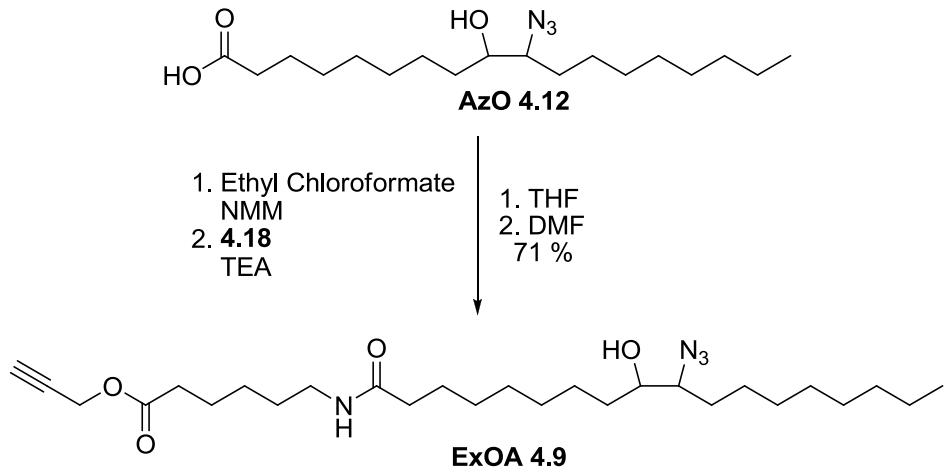
In order to test the effect of increasing potential intermolecular hydrogen bonding between polymer chains, a series of fatty amides **4.9** were synthesised. Short chained amides, similar to the propargyl ester controls **4.7** would have been the first choice for preparation, however due to expense of the propargylamine starting material these derivatives were not prepared. Consequently, derivatives of the extended series **4.8** were prepared, differing only in the atom of attachment. Prop-2-ynyl 6-aminohexanoate **4.18** was synthesised from 6-aminohexanoic acid **4.17** using thionyl chloride and propargyl alcohol (as reagent and solvent), at 10 °C for 20 mins followed by warming to room temperature for 30 mins (Scheme 4.5). Purification was achieved by trituration with hexane and afforded prop-2-ynyl 6-aminohexanoate **4.18** in 67 % yield.



Scheme 4.5: Synthesis of prop-2-ynyl 6-aminohexanoate 4.18.

Synthesis of ExOA **4.9**, ExLA **4.9**, ExRSA **4.9** and ExSBA **4.9** was achieved using the corresponding azido fatty acids **4.12** and reaction with prop-2-ynyl 6-

aminohexanoate **4.18** *via* a mixed anhydride method. Azido fatty acids **4.12** were reacted with ethyl chloroformate and *N*-methylmorpholine at 0 °C for 30 mins. *N*-methylmorpholine hydrochloride was removed and the fatty acid mixed anhydride was added dropwise to a solution of **4.18** and triethylamine in DMF at room temperature and stirred for 2 hours (Scheme 4.6). Purification through a silica plug (1:1 EtOAc: Hex) afforded ExOA **4.9**, ExLA **4.9**, ExRSA **4.9** and ExSBA **4.9** in 53 – 90 % yields.



Scheme 4.6: Synthesis of ExOA 4.9.

Mass spectrometry of the oleate monomer (Fig 4.19a) shows the mass ion peak at $[M+Na]^+$ 515.3 and a small percentage of epoxy oleate at $[M+Na]^+$ 472.2. The linoleic and triglyceride based monomers (Fig 4.19b-d) show the oleate monomer at $[M+Na]^+$ 516.3 and the linoleate monomer at $[M+Na]^+$ 572.3 and a small amount for 1 azido 1 epoxy linoleate side chain at $[M+Na]^+$ 529.3, a small peak can also be seen for epoxy oleate chains at $[M+Na]^+$ 473.3 in ExLA **4.9** ExRSA **4.9** and ExSBA **4.9** however less than that seen in **4.8** monomers. Both triglycerides show a small amount of palmitamide at $[M+Na]^+$ 430.2.

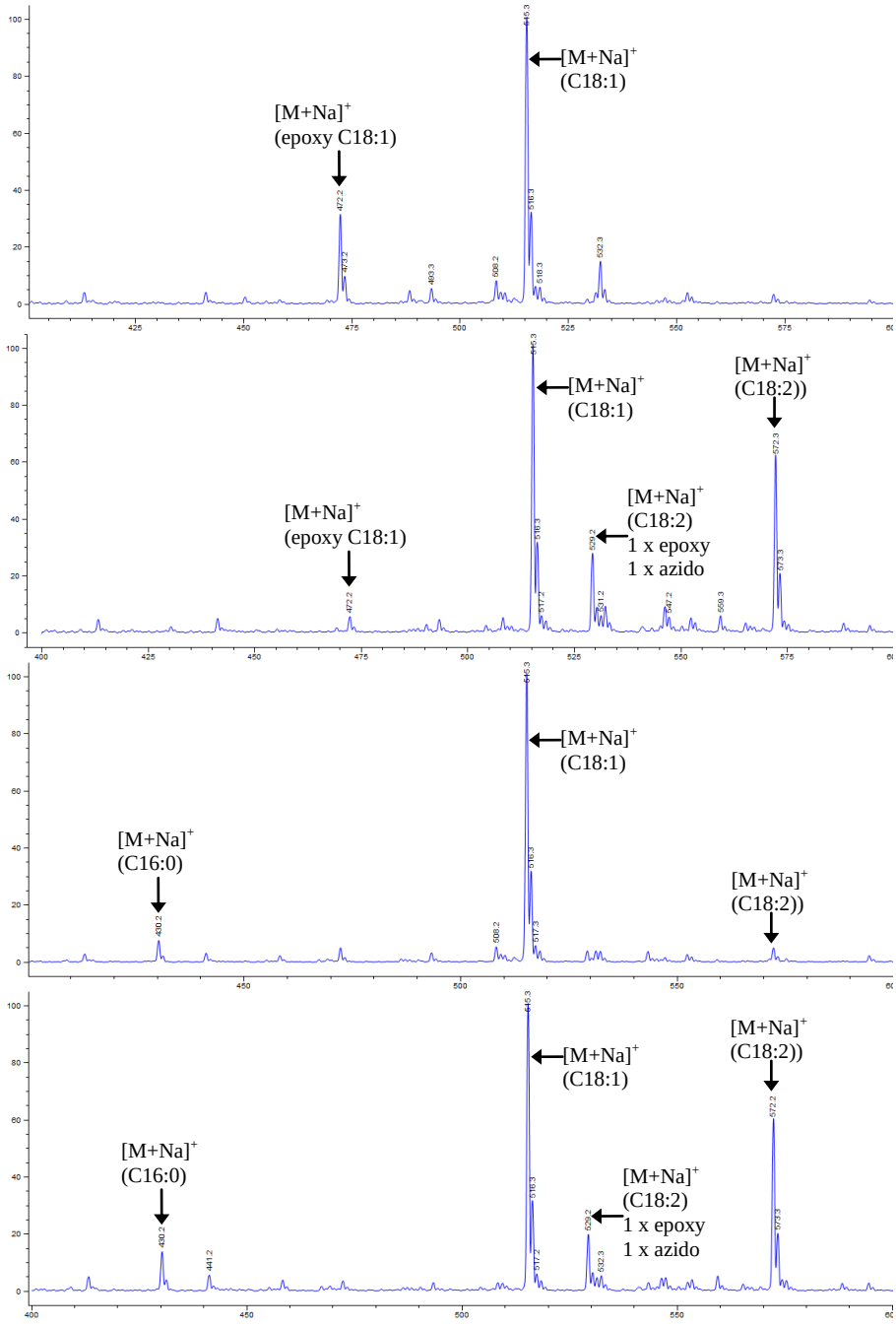


Figure 4.19: Mass spectra of ExOA 4.9, ExLA 4.9, ExRSA 4.9 and ExSBA 4.9 monomers.

The 400 MHz ^{1}H NMR spectra of OE **4.7**, ExOE **4.8** and ExOA **4.9** are recorded in Fig. 4.20.

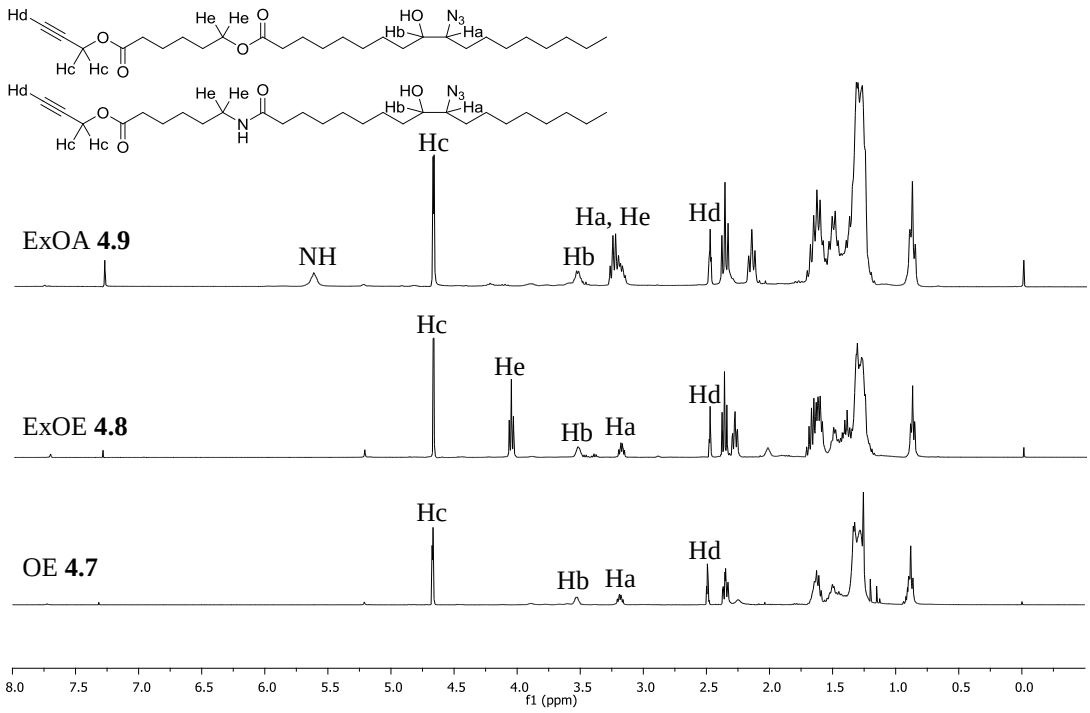


Figure 4.20: 400 MHz ^{1}H NMR spectrum control OE 4.7, extended ester monomer ExOE 4.8 and extended amide monomer ExOA 4.9.

4.5.2 Thermal analysis of extended amide monomers 4.9, and polymers 4.19.

Thermal analysis of the extended amide monomers **4.9** shows an increase in glass transition temperature (T_g) of 18 – 27 °C compared to the corresponding ester derivative **4.8**, this is caused by the increased intermolecular hydrogen bonding potential between the amide NH and the two carbonyl groups in the monomer structure (Table 4.8). Interestingly, apart from the linoleic acid derivatives, thermal stability of the extended amides ExOA **4.9**, ExRSA **4.9** and ExSBA **4.9** has decreased compared to the ester derivatives ExOE **4.8**, ExRSE **4.8** and ExSBE **4.8**. This was not expected as amides are generally more thermally stable than esters. T_{50} and T_{max} within the series are all within 8 °C, this effect is best seen in the soybean oil derivatives (Fig. 4.21).

Monomer	DSC (°C)[a]		TGA (°C)[a]		
	T_g	Cure Point	T_{10}	T_{50}	T_{max}
OE **4.7**	-61	161	339	400	479
LE **4.7**	-42	168	352	392	483
RSE **4.7**	-48	167	325	386	484
SBE **4.7**	-27	162	319	386	485
ExOE **4.8**	-68	163	336	393	492
ExLE **4.8**	-67	160	274	371	492
ERSE **4.8**	-64	161	332	395	500
ExSBE **4.8**	-58	155	309	392	498
ExOA **4.9**	-53	166	290	377	492
ExLA **4.9**	-38	157	301	382	496
ExRSA **4.9**	-46	161	325	385	488
ExSBA **4.9**	-32	155	294	383	488

[a] DSC and TGA values measured using 10 °C /min.

Table 4.8: Thermal comparison of monomer series 4.7, 4.8 and 4.9.

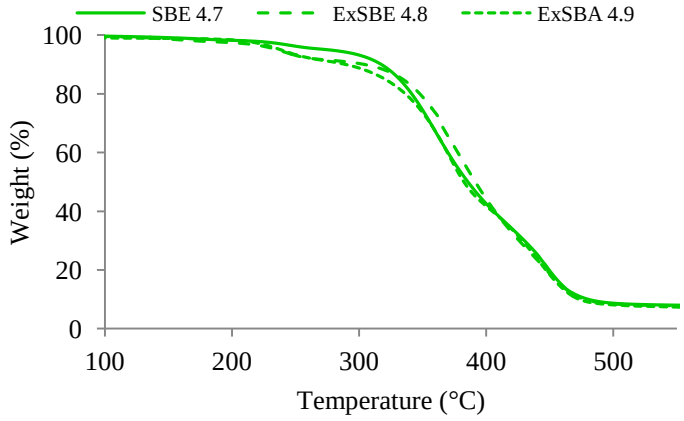


Figure 4.21: TGA comparison of monomers SBE 4.7, ExSBE 4.8 and ExSBA 4.9.

After polymerisation, thermal analysis again showed a large increase in T_g from monomer **4.9** to polymer **4.19**, (36 °C – 54 °C), (Fig 4.22). The presence of the amide group in the polymers **4.19** has increased the T_g between 16 °C – 22 °C (Fig 4.23) when compared to the corresponding ester derivatives **4.16** (Table 4.9).

However the thermal stability of the extended amide series **4.19** is again lower than the extended ester series **4.16**. Even though the presence of the amide increases the glass transition temperature by favourable hydrogen bonding, it causes a decrease in overall thermal stability. The reason for this is still unknown.

Polymer	DSC (°C)[a]	TGA (°C)[a]		
	T_g (°C)	T_{10}	T_{50}	T_{max}
POE **4.13**	-7	320	376	488
PLE **4.13**	21	325	390	491
PRSE **4.13**	1	323	385	477
PSBE **4.13**	22	319	387	481
PExOE **4.16**	-38	317	377	500
PExLE **4.16**	-3	338	387	500
PExRSE **4.16**	-14	329	383	483
PExSBE **4.16**	-1	339	397	488
PExOA **4.19**	-17	313	367	477
PExLA **4.19**	13	318	385	479
PExRSA **4.19**	8	326	377	479
PExSBA **4.19**	17	319	385	487

[a] DSC and TGA values measured using 10 °C /min.

Table 4.9: Thermal comparison of control 4.13, extended esters 4.16 and extended amides 4.19.

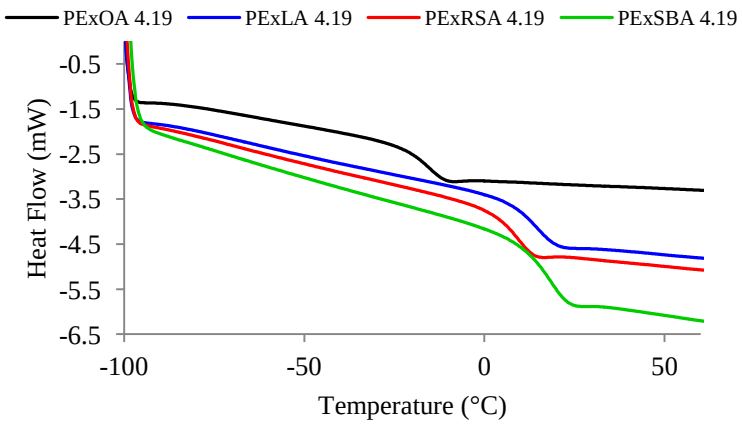


Figure 4.22: DSC comparison of polymers 4.19.

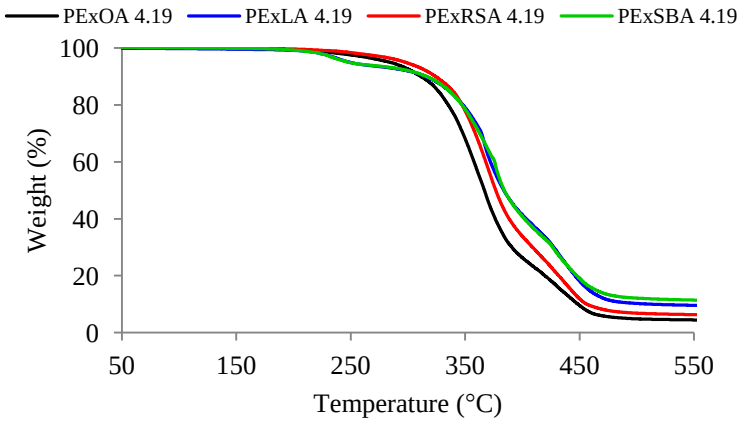


Figure 4.23: TGA comparison of polymers 4.19.

4.5.3 Mechanical testing of extended amide polymers 4.19

As for the extended ester series, the oleic derived material, PExOA **4.19** was too soft at room temperature to be mechanically tested, although the remainder in the series were investigated, (Table 4.10) (Fig 4.24a).

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa)[a]
POE **4.13**	0.1 (±0.02)	229 (±41)	0.1 (±0.03)
PLE **4.13**	5.1 (±0.78)	208 (±36)	2.7 (±0.04)
PRSE **4.13**	0.3 (±0.08)	658 (±36)	0.1 (±0.01)
PSBE **4.13**	0.6 (±0.13)	230 (±16)	0.3 (±0.10)
PExOE **4.16**	-	-	-
PExLE **4.16**	0.6 (±0.02)	176 (±2)	0.5 (±0.12)
PExRSE **4.16**	0.3 (±0.05)	454 (±54)	0.1 (±0.04)
PExSBE **4.16**	0.5 (±0.06)	292 (±35)	0.2 (±0.04)
PExOA **4.19**	-	-	-
PExLA **4.19**	0.9 (±0.08)	418 (±49)	0.4 (±0.02)
PExRSA **4.19**	0.7 (±0.38)	964 (±558)	0.3 (±0.04)
PExSBA **4.19**	0.6 (±0.21)	766 (±143)	0.2 (±0.02)

[a] UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. Values in brackets are error analysis based on standard deviation.

Table 4.10: Mechanical data comparison between the 4.13, extended ester 4.16 and amide 4.19.

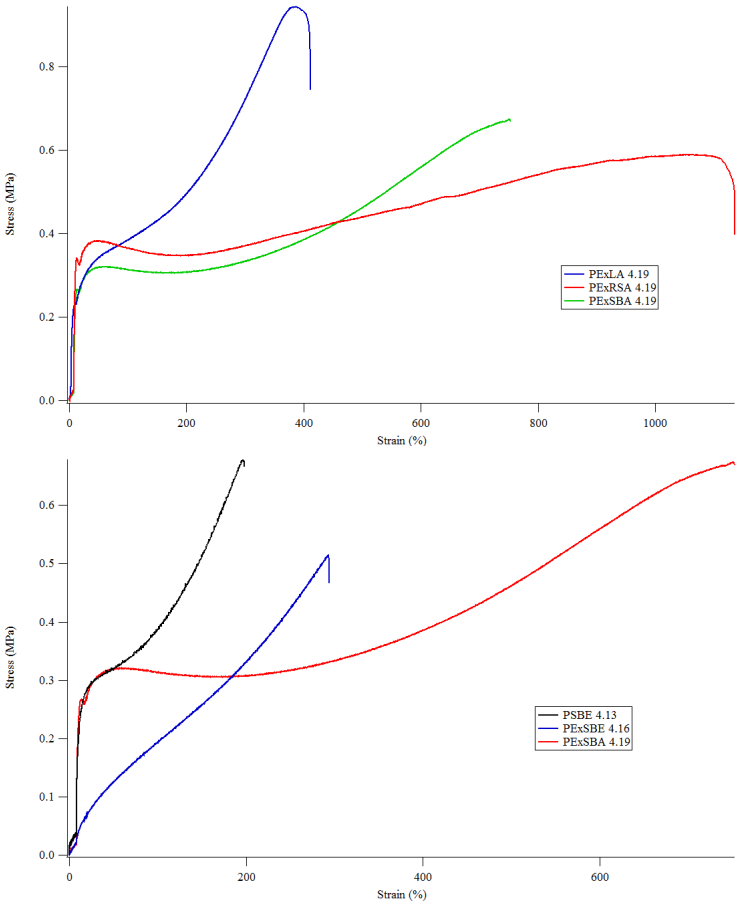


Figure 4.24: Stress-strain curve comparisons (a) PExLA 2.19, PExRSA 2.19 and PExSBA 2.19, (b) PSBE 4.13, PExSBE 4.16 and PExSBA 4.19.

Incorporation of the amide into the polymer network **4.19** has slightly increased the tensile strength and significantly increased the elongation at break compared to the extended ester derivatives **4.16** (*although the errors in measurement for PExRSA and PExSBA are significant*). As a result of the increased strength and increased elongation, the Youngs modulus remains similar to the extended ester **4.16** versions, showing the polymers have similar elastic properties however the amide would be more versatile, Figure 4.24b. PSBE **4.13** and PExLA **4.19** appear to show strain induced crystallisation, where an amorphous solid undergoes a phase transition

during the application of strain, as evident from the stress-strain curve showing a large increase in tensile strength after initial necking.

4.6 Effect of branching and cross-linking in homopolymers. Synthesis of monomers 4.10 and 4.11 derived from ethanolamine and diethanolamine.

Results from sections 4.3, 4.4 and 4.5 established:

- Increasing chain length decreases T_g of both monomers and polymers and decreases tensile strength of polymers.
- Increasing chain length increases elongation at break of polymers.
- Incorporation of an amide capable of H-bonding increases T_g of both monomers and polymers and increases the tensile strength and elongation of polymers.

The effect of increasing branching possibilities within polymer networks by incorporating two alkyne groups per monomer **4.11** (derived from diethanolamine) was investigated next. In this monomer series the alkyne groups are attached by ether linkages and the amide is tertiary in nature (no H-bond donor ability). As a comparison the ether linked **4.10** derived from ethanolamine which contains only one alkyne group but a secondary amide capable of H-bond donation was also prepared, (Fig. 4.25).

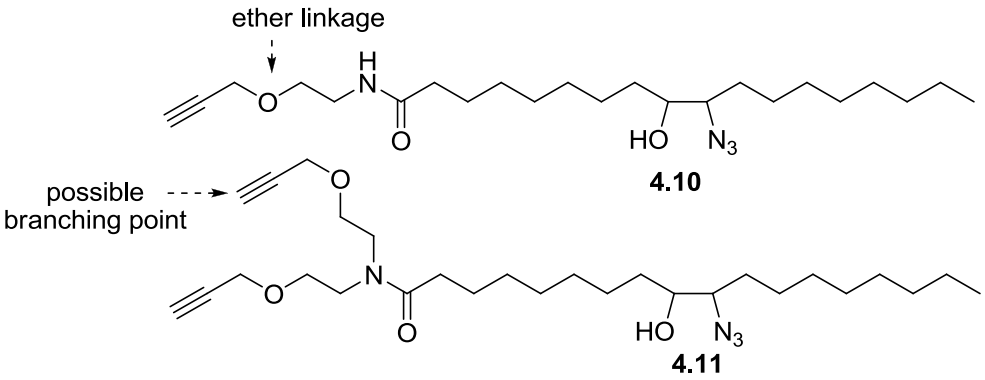
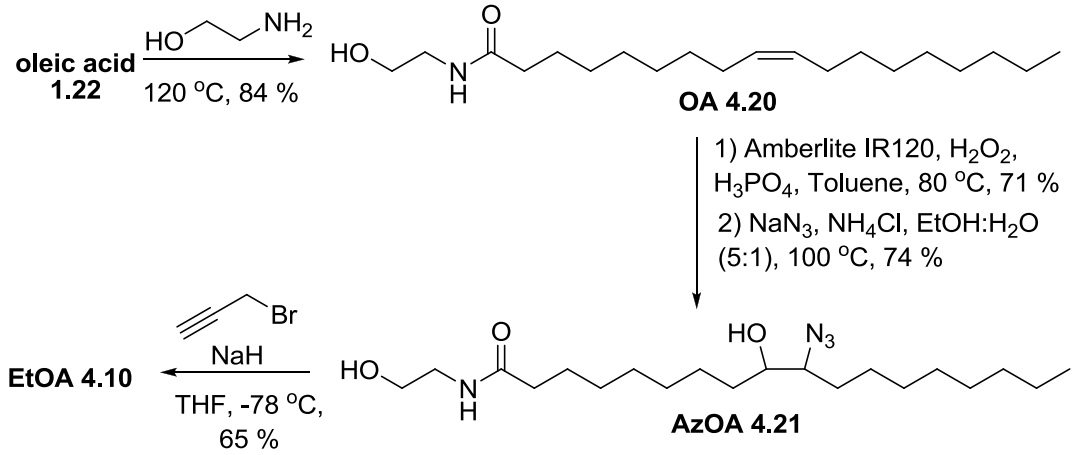


Figure 4.25: Monomer series 4.10 and 4.11

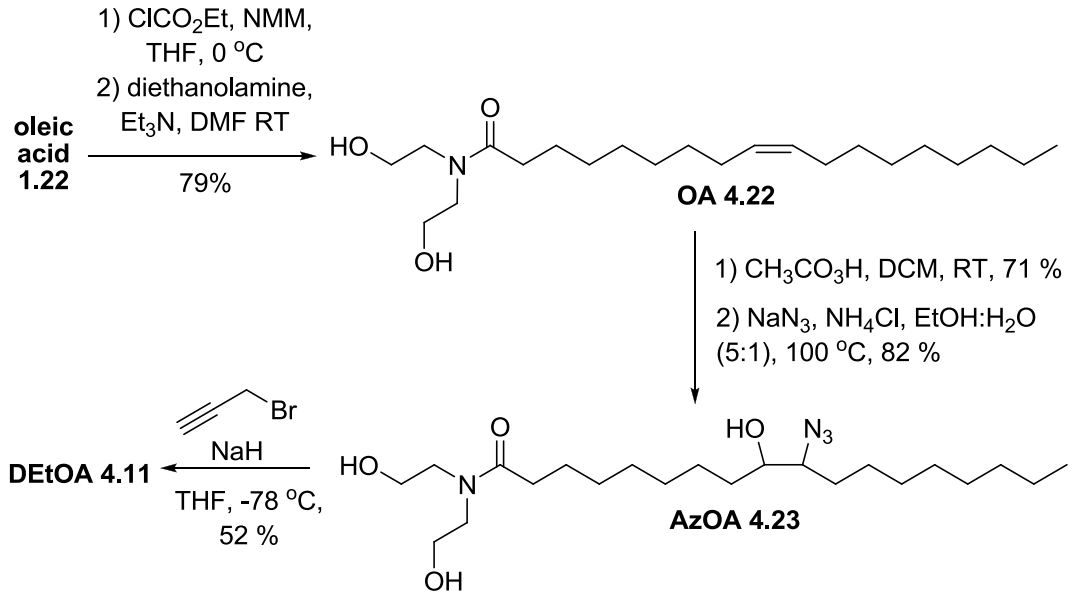
4.6.1 Synthesis of monomer series 4.10 and 4.11.

Ethanolamine was incorporated into fatty acids and hydrolysed triglycerides using a condensation reaction where both reactants were heated to 120 °C for 24 hours. This furnished amides **4.20** in 83 – 84 % yields. Epoxidation and azidation was achieved using the same protocols described in section 4.3 to give **4.21** which was alkynated using NaH and propargyl bromide in THF at -78 °C for 30 mins to give **4.10** in 44 – 87 % yields (Scheme 4.7). The azide values were determined (EtOA **4.10** = 0.7, EtLA **4.10** = 0.8, EtRSA **4.10** = 0.9, EtSBA **4.10** = 1.1).



Scheme 4.7: Synthesis of EtOA 4.10.

The diethanolamine series **4.11** was prepared in a different manner. Diethanolamine was incorporated into fatty acids using the ethyl chloroformate method used in section 4.5.1 and gave **4.22** in 78-91% yields after purification.



Scheme 4.8: Synthesis of DEtOA 4.11.

Epoxidation was attempted using the Amberlite® method however only starting materials were recovered. Epoxidation was subsequently achieved using peracetic acid in DCM for 16 hours and azidation was achieved using the same protocol as before giving **4.23** 62 – 85 % yields. Dialkylation was achieved with NaH and propargyl bromide affording DEtOA **4.11**, DEtLA **4.11**, DEtRSA **4.11** and DEtSBA **4.11** in 26 – 52 % yields (Scheme 4.8).

Mass spectrometry of the ethanolamine monomers (Fig 4.26a) shows the mass ion peak at $[M+Na]^+$ 445.2 for the oleic monomer and a small percentage of epoxy oleate at $[M+Na]^+$ 402.2. The linoleic and triglyceride based monomers (Fig 4.26b-c, Fig 4.27) show the oleate monomer at $[M+Na]^+$ 445.2 and the linoleate monomer

at $[M+Na]^+$ 502.2 and a small amount for 1 azido 1 epoxy linoleate side chain at $[M+Na]^+$ 459.2, a small peak can also be seen for epoxy oleate chains at $[M+Na]^+$ 402.2 in EtLA **4.10** EtRSA **4.10** and EtSBA **4.10**. Both triglycerides show a small amount of monomer with a propargyl group attached to the secondary alcohol next to the azide functionality at $[M+Na]^+$ 540.2 in the linoleic chain and $[M+Na]^+$ 483.2 in the oleic chain.

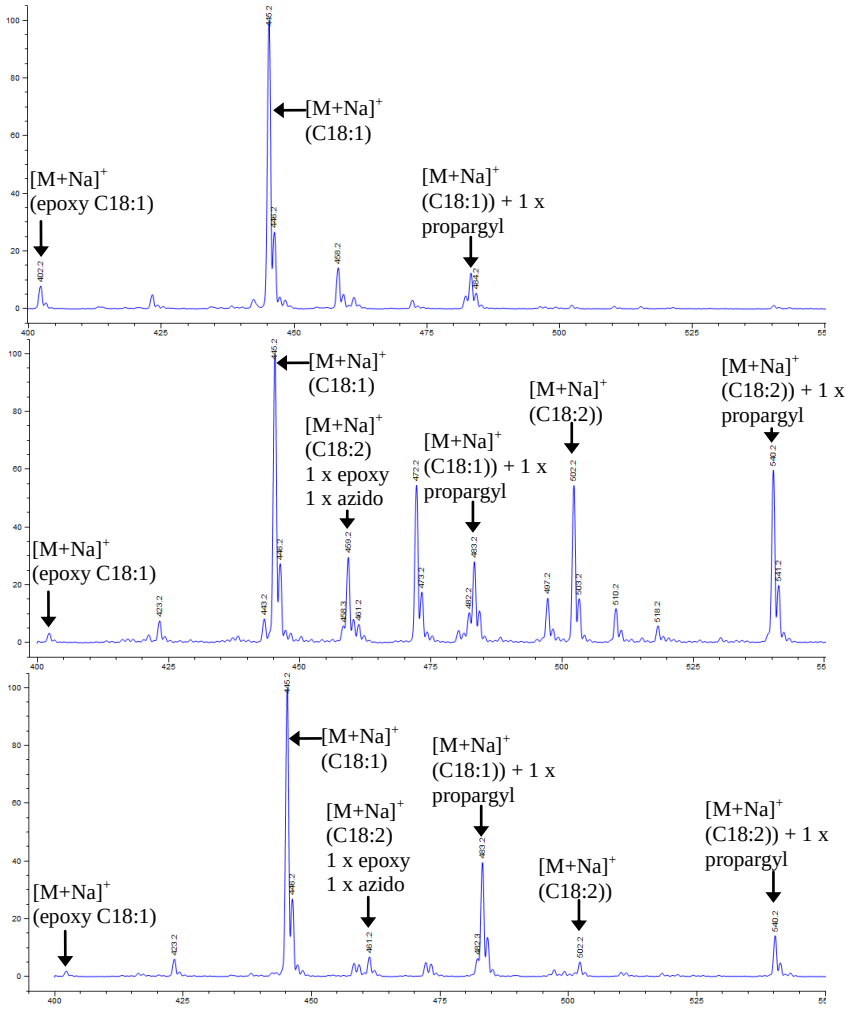


Figure 4.26: Mass spectra for (a) EtOA 4.10, (b) EtLA 4.10 and (c) EtRSA 4.10 monomers.

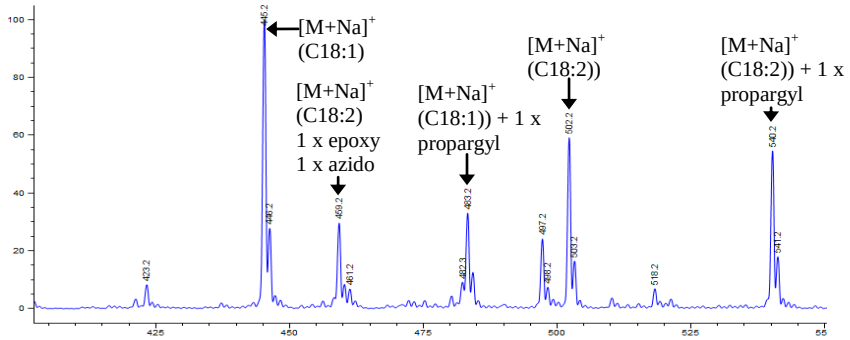


Figure 4.27: Mass spectrum of EtSBA 4.10 monomer.

Mass spectrometry of the diethanolamine monomers (Fig 4.28) shows the mass ion peak at $[M+Na]^+$ 527.2 for the oleic monomer and a small percentage of epoxy oleate at $[M+Na]^+$ 484.2. The linoleic and triglyceride based monomers (Fig 4.29a-c) show the oleate monomer at $[M+Na]^+$ 527.2 and the linoleate monomer at $[M+Na]^+$ 584.2. Again a small mass ion peak can be seen for 1 azido 1 epoxy linoleate side chain at $[M+Na]^+$ 541.2 and a small peak can also be seen for epoxy oleate chains at $[M+Na]^+$ 484.3 in DEtLa **4.11** DEtRSA **4.11** and DEtSBE **4.11**. Both triglycerides show a small amount of monomer with a propargyl group attached to the secondary alcohol next to the azide functionality at $[M+Na]^+$ 622.2 in the linoleic chain and a smaller peak $[M+Na]^+$ 565.2 in the oleic chain. Again a mass ion peak can be seen at $[M+Na]^+$ 442.2 for the palmitamide with propargyl groups attached.

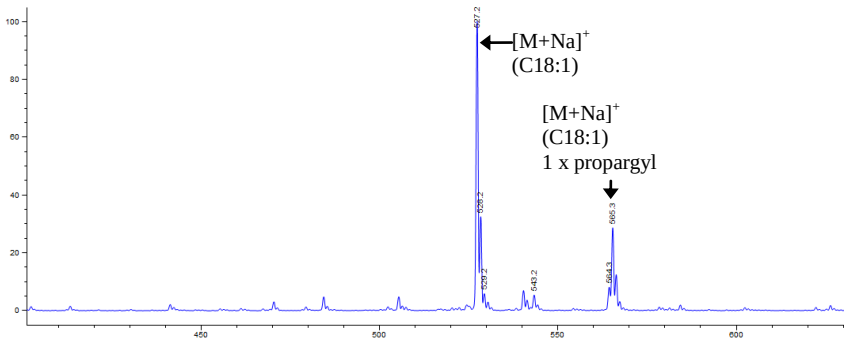


Figure 4.28: Mass spectrum of DEtOA 4.11 monomer.

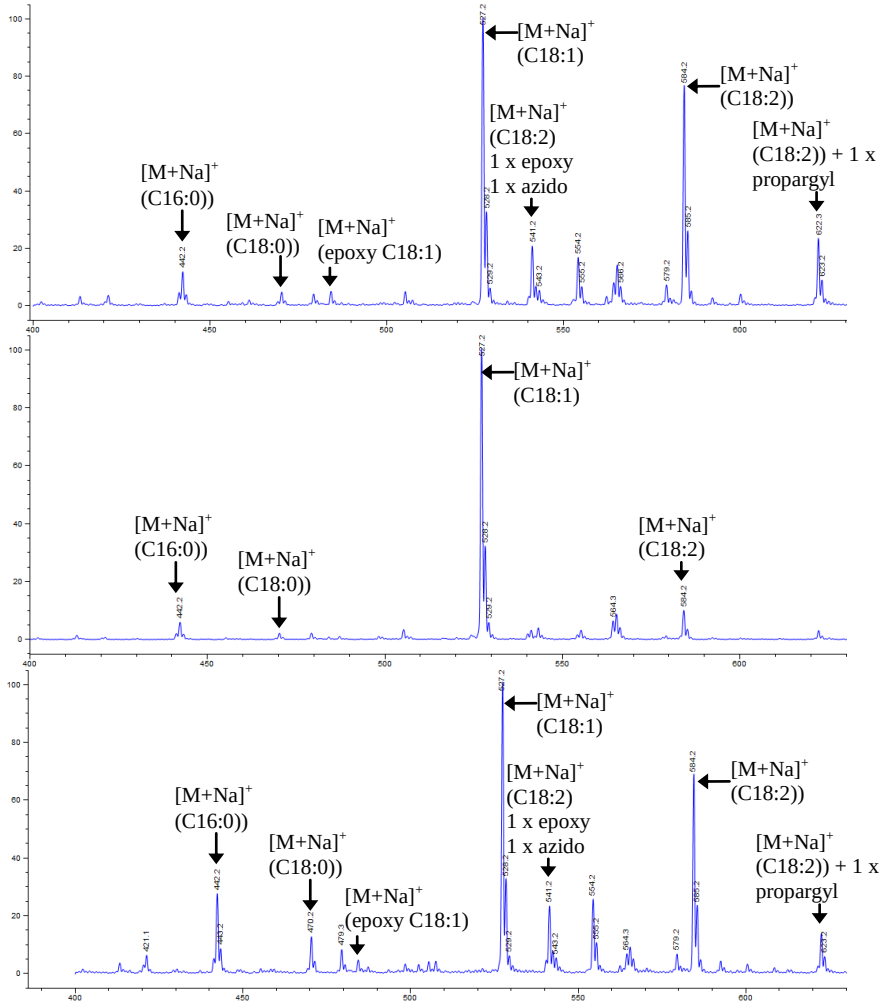


Figure 4.29: Mass spectra of (a) DEtLA 4.11, (b) DEtRSA 4.11 and (c) DEtSBA 4.11 monomers.

4.6.2 Thermal analysis of monomers and polymers derived from 4.10 and 4.11

Despite the branched nature of the tertiary amides **4.11** DSC analysis shows a decrease (3 – 7 °C) in glass transition temperature (T_g) with respect to the ethanolamine derived series **4.10**, (Table 4.12). Presumably, the loss of the amide NH group, which participates as a H-donor, is more important than the extra branching in this series. In both series, the lower T_g values are found for the monomers containing higher levels of oleic acid derived chains (EtOA **4.10**, EtRSA **4.10**, and DEtOA **4.11**, DEtRSA **4.11)** with the monomers containing the highest component of linoleic side chains having the highest T_g values (EtLA **4.10** and

DEtLA **4.11**). Thermal stabilities are similar between both series for molecules derived from the same oil. Interestingly, the thermal stability of the ethanolamine based amides is higher than the 6-aminohexanoic acid based amides (e.g. *EtLA **4.11** T_{10} = 335 °C, ExLA **4.10** T_{10} = 301 °C, ΔT_{10} = 34 °C*) and also shows a narrower degradation range, presumably due to the replacement of the ester groups with ether groups (Table 4.11).

Monomer	DSC (°C)[a]		TGA (°C)[a]		
	T_g	Cure Point	T_{10}	T_{50}	T_{max}
EtOA **4.10**	-41	168	336	389	486
EtLA **4.10**	-33	163	335	398	495
EtRSA **4.10**	-44	164	342	395	487
EtSBA **4.10**	-38	161	313	397	492
DEtOA **4.11**	-49	157	339	383	489
DEtLA **4.11**	-39	158	329	394	486
DEtRSA **4.11**	-48	158	328	391	489
DEtSBA **4.11**	-41	159	315	388	494

[a] DSC and TGA values measured using 10 °C /min

Table 4.11: Comparison of thermal data of ethanolamine 4.10 and diethanolamine amides 4.11.

After successful polymerisation, using the same method as described in section 4.3, thermal analysis of the resultant polymers **4.24** and **4.25** show a large increase in glass transition temperature compared to their monomers, ΔT_g ranges from +16 °C (DEtRSA **4.11** → PDEtRSA **4.25**) to + 73°C (DEtLA **4.11** → PDEtLA **4.25**), (Table 4.12). Polymers prepared from monomers with high linoleic content PEtLA **4.24** and PDEtLA **4.25**) have much higher T_g values (above RT) than those derived mainly from oleic chains (PEtOA **4.24** and PDEtOA **4.25**), for the reasons already alluded to in other chapters. The thermal stabilities for the more branched polymers **4.25** are generally lower than for the corresponding unbranched materials **4.24**. Examining the TGA profiles, (Fig. 4.30) for series **4.25** note the absence of an initial

decomposition at about 250 °C corresponding to unreacted azide groups. This is to be expected, as for this series the alkyne reactive groups were in excess and will be available for further reaction after polymerisation if required.

Polymer	DSC (°C)[a]	TGA (°C)[a]		
	T_g	T_{10}	T_{50}	T_{max}
PEtOA **4.24**	-2	349	401	482
PEtLA **4.24**	35	342	403	489
PEtRSA **4.24**	-1	353	405	483
PEtSBA **4.24**	35	340	410	487
PDEtOA **4.25**	-17	316	388	477
PDEtLA **4.25**	34	339	409	479
PDEtRSA **4.25**	-32	340	389	483
PDEtSBA **4.25**	18	335	385	488

[a] DSC and TGA values measured using 10 °C /min

Table 4.12: Thermal data for ethanolamine 4.24 and diethanolamine 4.25 derived polymers.

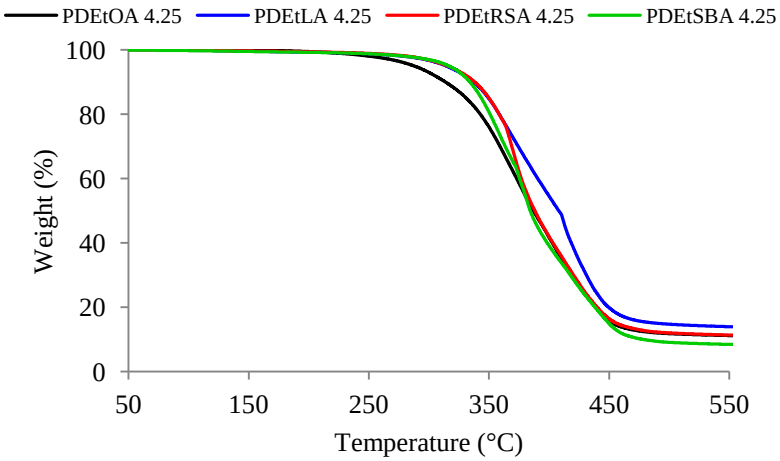


Figure 4.30: Thermal data for diethanolamine 4.25 derived polymers.

4.6.3 Mechanical testing of polymers 4.24 and 4.25

PEtLA **4.24** PEtSBA **4.24** and PDEtLA **4.25** PDEtSBA **4.25** were successfully mechanically tested (Table 4.13) (Fig 4.31).

Polymer	UTS (MPa)[a]	EaB (%)[a]	YM (MPa) [a]
PEtOA **4.24**	-	-	-
PEtLA **4.24**	36.4 (±4.17)	20 (±11)	425.5 (±51.89)
PEtRSA **4.24**	-	-	-
PEtSBA **4.24**	28.7 (±8.94)	20 (±11)	256.8 (±97.64)
PDEtOA **4.25**	-	-	-
PDEtLA **4.25**	14.7 (±1.90)	61 (±7)	46.1 (±9.38)
PDEtRSA **4.25**	-	-	-
PDEtSBA **4.25**	2.7 (±0.21)	148 (±8)	1.6 (±0.02)

[a] UTS = ultimate tensile stress, EaB = elongation at break and YM = Young's modulus. Results obtained using Instron 5800R at rate of 1 mm/min for 2 mm then 10 mm/min until break. Values in brackets are error analysis based on standard deviation.

Table 4.13: Mechanical data comparison between 4.25 and 4.26 derived polymers.

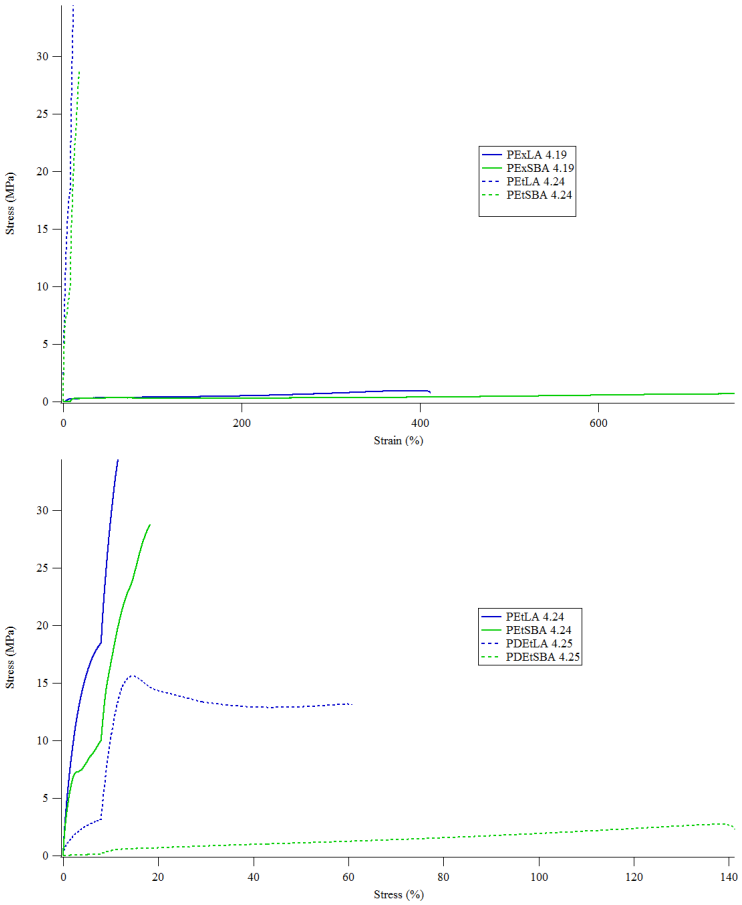


Figure 4.31: Tensile comparison of (a) PExLA 4.19, PExSBA 4.19, PEtLA 4.24 and PEtSBA 4.24. (b) PEtLA 4.24, PEtSBA 4.24, PDEtLA 4.25, and PDEtSBA 4.25.

Interestingly, increasing the number of alkyne units (and hence encouraging cross-linking for linoleic derived materials with azide numbers > 1) did not seem to

increase the tensile strength but instead decreased it, (Fig. 4.31(b)). The reasons are unclear, but it seems that the loss of the NH group and hence a H-bonding donor interaction is far more important in controlling the T_g and tensile strength than the ability to cross-link *via* an additional alkyne unit. This may be because the azide values in these monomers are low and the ability to cross-link is not as great as a consequence. As seen in this and earlier chapters, PEtLA and PEtSBA **4.24** show yield hardening where the polymer is strengthened by dislocations within the crystal structure of the polymer, i.e. where the polymer chains slide past each other increasing packing and strength of the polymer. Necking can again be seen in PDEtLA **4.25** however this is not followed by strain hardening and leads ultimately to fracture of the polymer.

4.7 Summary and Conclusion

Homopolymers were successfully synthesised from all sets of monomers **4.7**-**4.11**. Initial polymers were based upon monomer **4.7** and furnished oleic acid (POE **4.13**), linoleic acid (PLE **4.13**), rapeseed oil (PRSE **4.13**) and soybean oil (PSBE **4.13**). POE **4.13** had the lowest glass transition temperature in the series (*POE **4.13** Tg = -7 °C*) and lowest tensile strength (*POE **4.13** UTS = 0.1 MPa*). Changing to a more unsaturated chain derivative (linoleic) and therefore greater azide functionality and H-bonding opportunities increased both T_g and tensile strength. Increasing the distance between the reacting alkyne and azide functionalities causes a decrease in T_g and tensile strength with elongation at break also showing a slight decrease. The oleic acid derived polymer PExOE **4.16** became too soft at room temperature to

mechanically test. The Youngs moduli of the extended polymers, PExOE **4.16**, PExLE **4.16**, PExRSE **4.16** and PExSBE **4.16**, has decreased showing the polymers are more elastic than the short chained esters **4.13** (P*ExLE* ***4.30*** *YM = 0.5 MPa, PLE* ***4.13*** *YM = 2.7 MPa, ΔYM = 2.2 MPa*). This confirms the hypothesis of increasing chain length causing a decrease in the thermal and mechanical properties of this class of polymer and agrees with the similar effect noted in chapter 3.

Modification of the extended esters **4.16**, to amides **4.17**, increases the glass transition temperatures, tensile strengths and elongation at break of the polymers due to increased hydrogen bonding opportunities. Glass transition temperatures increase on average 19 °C within the series (P*ExOA* ***4.19*** *Tg = -17 °C, PExOE* ***4.16*** *Tg = -38 °C, ΔTg = 21 °C*), tensile strength increases 0.3 MPa on average within the series (P*ExLA* ***4.19*** *UTS = 0.9 MPa, PExLE* ***4.16*** *UTS = 0.6 MPa, ΔUTS = 0.3 MPa*) and elongation increases to over two times the length of the extended ester series (P*ExRSA* ***4.19*** *EoB = 964 %, PExRSE* ***4.16*** *UTS = 454 %, ΔEoB = 510 %*) and subsequently means the elasticity remains similar to the extended ester series.

Ethanolamine based homopolymers **4.24** show an increase in thermal properties and an increase in tensile strength (P*ExLA* ***4.19*** *UTS = 0.9 MPa, PEtLA* ***4.24*** *UTS = 36.4 MPa, ΔUTS = 35.5 MPa*) however, elongation at break decreases drastically due to T_g of the polymers **4.24** being above the temperature at which they were tested making them more glass-like, therefore less elastic and more brittle (*PEtLA* ***4.24*** *EoB = 20 %, PExLA* ***4.19*** *EoB = 418 %, ΔEoB = -398 %*). Removal of some hydrogen bonding ability and addition of a branching possibility **4.24** → **4.25** causes a decrease in glass transition temperature, tensile strength (*PEtLA* ***4.24*** *UTS = 36.4 MPa, PDEtLA* ***4.25*** *UTS = 14.7 MPa, ΔUTS = -21.7 MPa*) and elasticity, however

increases elongation at break of the polymers (*PEtLA* ***4.24*** *EoB = 20 &, PDEtLA* ***4.25*** *EoB = 60 %, ΔEoB = 40 %*).

In all cases, all monomers derived from triglycerides (rapeseed and soybean) have shown lower values for T_g, UTS, EoB and YM than those derived from commercially available oleic acid and linoleic acid. This is due to the increased amount of saturation within the triglycerides (less azide number) causing premature termination of the polymer networks.

4.8 Future Work

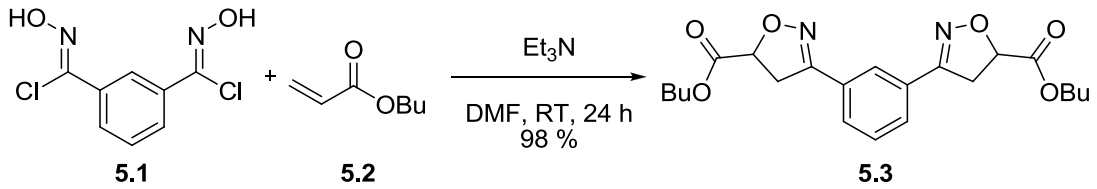
As suggested by Scheel *et al*. and demonstrated by Li *et al*. having extra azide or alkyne functionality present after polymerisation could lead to further end group modification, this suggests two possibilities for further work.[133,205] With the statistical mixtures of the fatty acids **4.7-4.11** containing 1.0-1.5 azide groups when fully ring-opened, the remaining post polymerisation surface azide groups can be further modified in subsequent click reactions to improve properties and cross-linking. Alternatively, the remaining post polymerisation alkyne groups present in materials derived from diethanolamine **4.25** can be further functionalised. Further click reactions could cause an increase in glass transition temperatures, if imparting extra hydrogen bonding, or cross-linking.

Having also seen, in the work by Li *et al.,* the hyperbranched polymers had nonlinear optical properties it would be interesting to test the polymers synthesised in this chapter and establish if any have potential to be nonlinear optical polymeric materials derived from renewable sources.

5.0 Synthesis of Renewable Alkyne-Nitrile Oxide Click Polymers.

5.1 Introduction

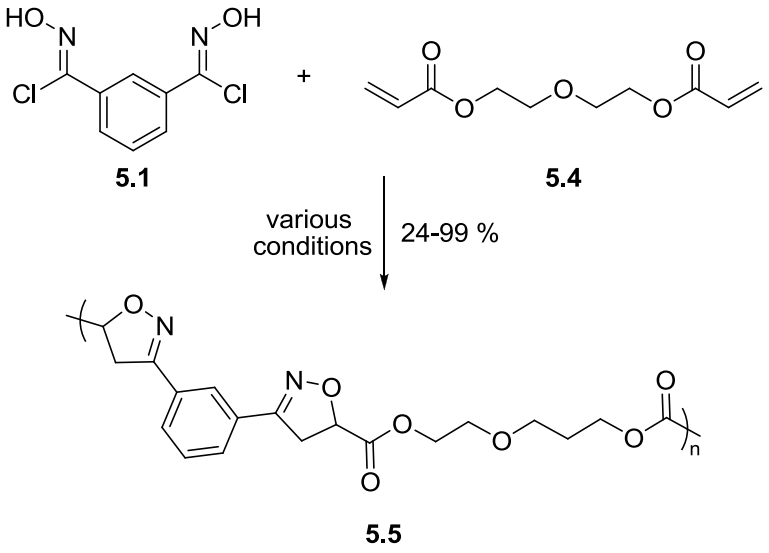
As has already been described in previous chapters, the Huisgen cycloaddition of azides with alkynes has been used extensively in the field of polymer chemistry,[136] although the use of it to prepare renewable materials has received less attention.[138-139] A major disadvantage of the Huisgen cycloaddition is the use of toxic and explosive azides and the need for Cu catalysis for some approaches. The use of the related nitrile oxide-alkyne click reaction to prepare polyisoxazoles is less common,[146,153-154,206-211] and from literature review has never been applied to the preparation of renewable polymers. In 2009 Takata *et al.* attempted the synthesis of polymers from dialkene and dialkyne substrates with dinitrile oxides prepared *in situ* by the elimination of HCl from **5.1**.[153] A simple system involving heating isophthalohydroximoyldichloride **5.1** and butyl acrylate **5.2** with a base in DMF was initially studied, (Scheme 5.1), and 1,3-bis(3-isoxazolinyl)benzene **5.3** was obtained in 98 % yield as a single 3,5-disubstituted regioisomer **5.3**, although no information on the diastereoselectivity of the reaction was reported.



5.1 **5.2** **5.3**

Scheme 5.1: Reaction of 5.1 and butyl acrylate 5.2.

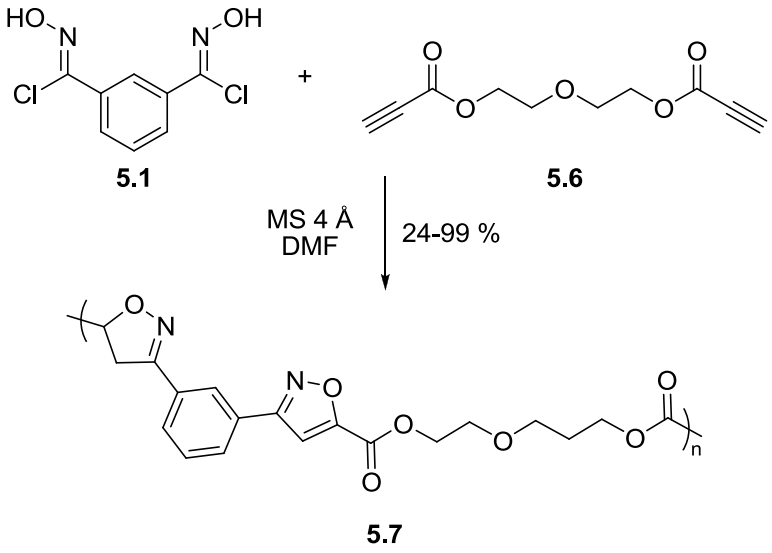
Using this knowledge polymerisations were attempted, initially using 2,2'-oxybis(ethane-2,1-diyl) diacrylate **5.4**, with a range of bases and solvents to produce polyisoxazoline **5.5**, (Scheme 5.2). The best conditions found used sodium hydroxide in DCM and water with a small amount of a phase transfer catalyst at room temperature (*base method*) or using DMF with 4 Å molecular sieves at 100 °C (*thermal method*). Both approaches gave high yields of polymer **5.5** in 24 hours (99%), however, the thermal method produced higher molecular weight polymers (*NaOH DCM:H_2O = 4600 Mw, MS 4 Å DMF = 14900 Mw*).



Scheme 5.2: Synthesis of polyisoxazoline 5.5.

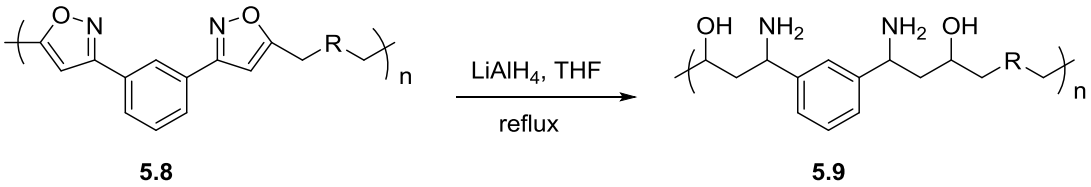
Further polymerisations were attempted using the thermal method. A range of monomers were studied including the alkyne analogue **5.6**, which upon polymerisation with **5.1** produced polyisoxazole **5.7**, (Scheme 5.3). Lower molecular weights of polyisoxazole **5.7** compared to polyisoxazoline **5.5** were obtained (*polyisoxazoline **5.5** = 14900 Mw, polyisoxazoles **5.7** = 1900*) due to the

generally lower solubility of isoxazoles compared to isoxazolines facilitating precipitation of **5.7** during the polymerisation.



Scheme 5.3: Synthesis of polyisoxazole 5.7.

The following year Takata *et al.* expanded on this research by synthesising a series of polymers from dialkynes with a range of chain lengths, utilising diaromatic and polyether backbones.[154] The polymers were synthesised in 84 – 98 % yields and had a range of molecular weights, ranging from 2300 Mw, for those synthesised from straight alkyl chained dialkynes, to 419300 Mw for the polymers containing poly 1,4-butylene glycol. Reduction of the polyisoxazoles **5.8** to poly(β-aminoalcohols) **5.9** was accomplished using $LiAlH_4$ in THF at reflux, (Scheme 5.4). Polyamines are important materials that can be used as ion channels, gene delivery vectors or ion exchange resins.[211-213] The derived poly(β-aminoalcohols) **5.9** could be cross-linked either with terephthalaldehyde or methylene diphenyldiisocyanate (MDI) to form cross-linked polymers.



5.8 **5.9**

Scheme 5.4: Reduction of polyoxazoles 5.8 to give poly(β-aminoalcohols) 5.9 with $LiAlH_4$.

In summary, they found:

- Nitrile oxide-click polymers could be produced from a range of alkyl and aromatic based dialkenes and dialkynes, with those from dialkynes having lower molecular weights than those derived from dialkenes.
- Polymerisation was successful using a) the *thermal method* (100 °C) in the presence of molecular sieves or b) the *base method* promoted at room temperature. In general higher molecular weights were found for polymers produced by the thermal method.
- Thermal onset of degradation was approximately 245 °C for polymers prepared using the thermal method, however comparison studies between both approaches were not reported.
- Reduction of the polyisoxazoles **5.8** with $LiAlH_4$ furnished versatile poly(β-aminoalcohols) **5.9** which could be further cross-linked and have the potential to be useful scaffolds for a variety of applications.

5.2 Aims and Objectives

Inspired by the work of Takata *et al.* investigations into whether alkyne derived monomers **5.11** prepared from renewable oils (e.g. oleic acid) could be successfully

used to prepare polyisoxazoles using nitrile oxide-click chemistry and whether the unsaturated nature of the fatty acid *cis* alkene increased the chances of cross-linking *via* isoxazoline rings, (Fig. 5.1) were carried out.

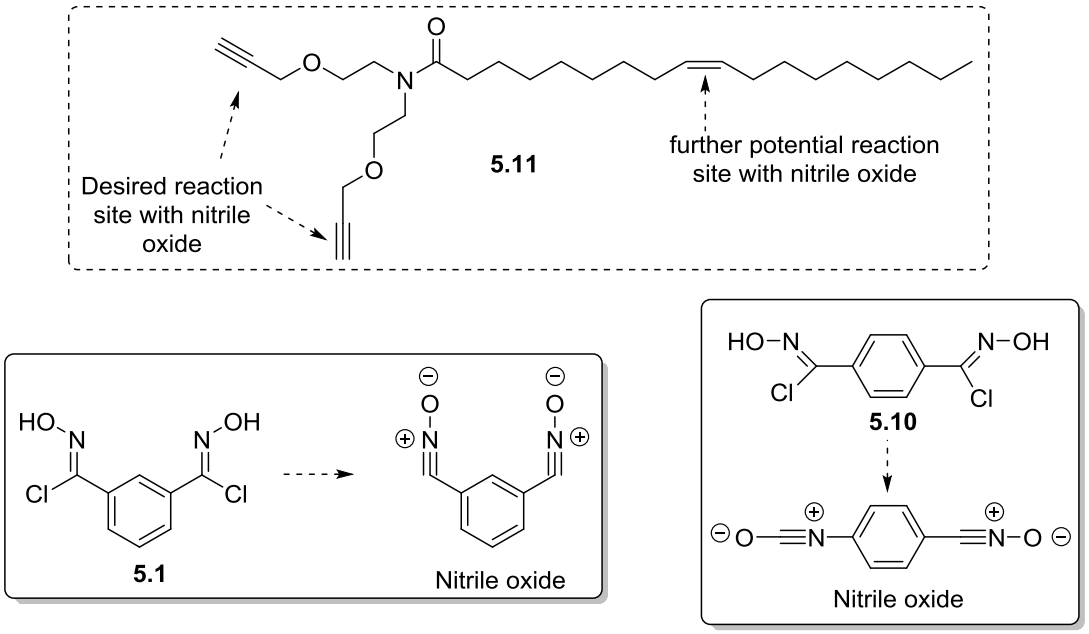


Figure 5.1: Structures of monomer 5.11 and nitrile oxide precursors 5.1 and 5.10.

Additional investigations were undertaken to establish:

- If the thermal properties and molecular weights of polyisoxazoles prepared from renewable oils showed any significant difference depending upon their method of preparation (*thermal method* or *base method*) as reported in Takata's papers, and if so whether they paralleled that observed when using the thermal or copper catalysed methods for the synthesis of the related azide-click polymers, (see Chapter 3).
- The effect on the properties of any prepared polymers using a linear dinitrile oxide precursor, terephthalohydroximoyl dichloride **5.10** compared to isophthalohydroximoyldichloride **5.1**. While Takata *et al.* had reported the

use of **5.10** in his chemistry no comprehensive thermal studies were carried out as to the effects on the thermal properties of materials incorporating it.

To this end, a series of dialkynes derived from a) commercially available oleic **5.11**, (Fig. 5.1) and linoleic acids **5.12**, (Fig. 5.2), b) the fatty acids derived from hydrolysis of industrially available triglycerides, rapeseed oil **5.13** and soybean oil **5.14**, (not shown) as well as c) a polyalkynated soybean oil **3.1**, (Fig. 5.2) were prepared. Thus, assessments could be made into the effect of the number of alkenes in the monomers on the properties of the polymers (comparing **5.11** vs **5.12**), the number of alkynes in the monomers (comparing **5**.**11** and **5.12** vs **3.1**), and the effect of using a cheaper but more polydisperse mixture of fatty acids as monomers (comparing **5.13** vs **5.11** and **5.14** vs **5.12**).

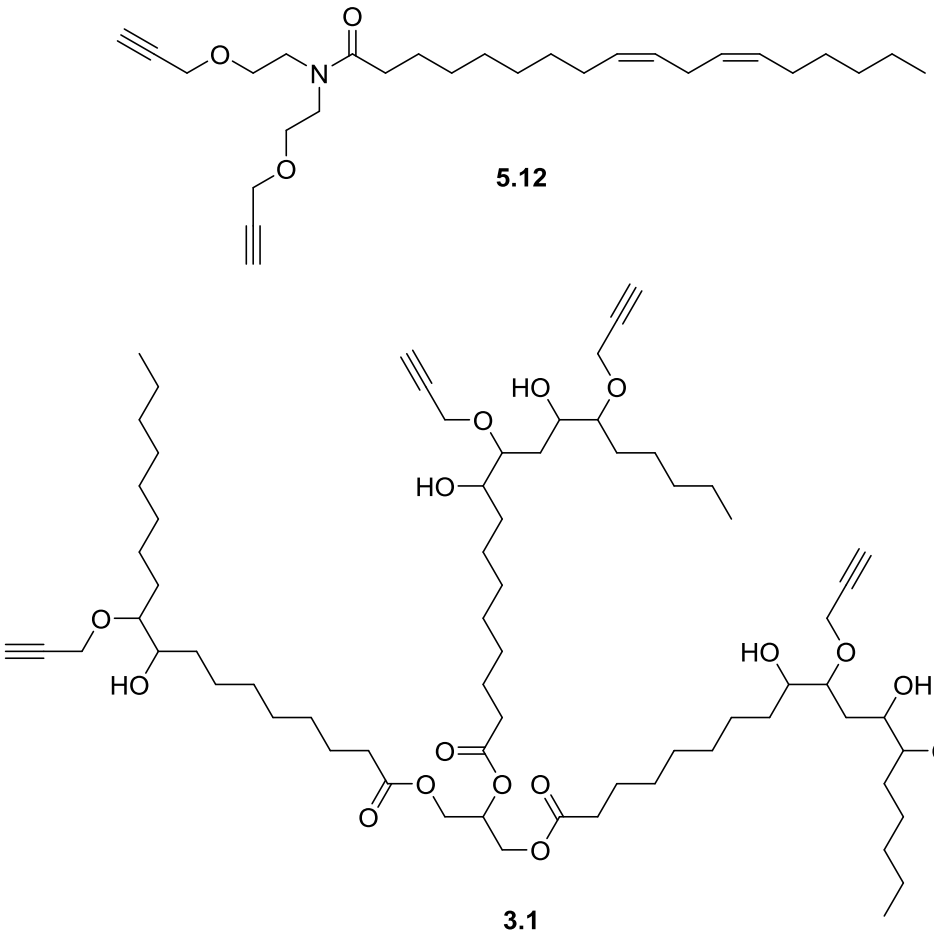


Figure 5.2: Monomers from linoleic acid 5.12 and polyalkynated soybean oil 3.1.

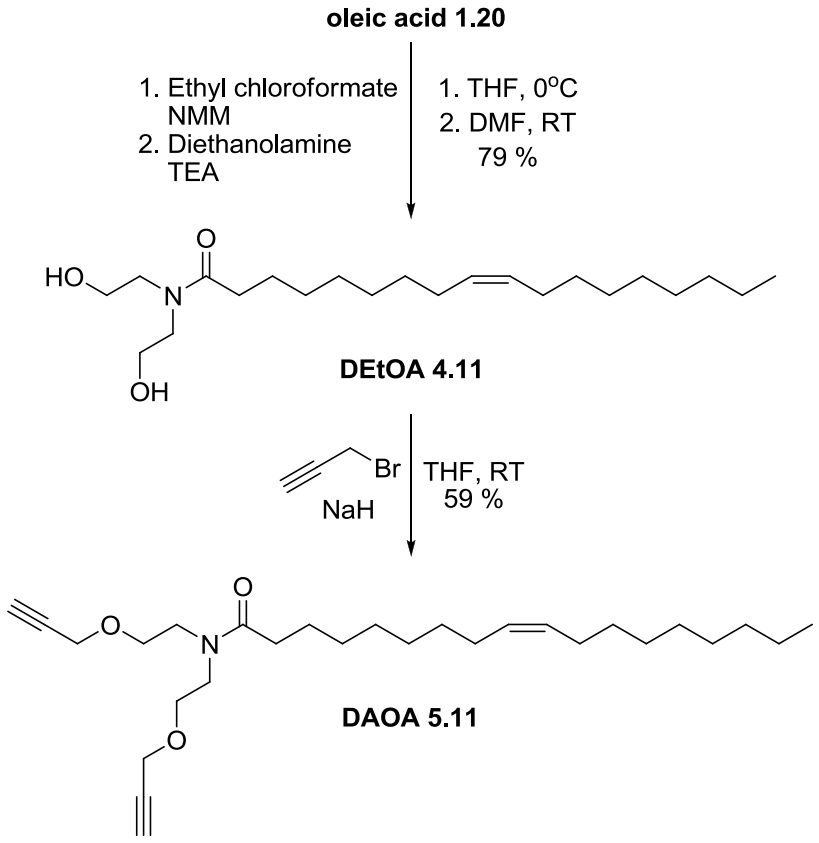
In addition, the polymerisation reaction of each monomer with nitrile oxide precursors, isophthalohydroximoyldichloride **5.1** and terephthalohydroximoyl dichloride **5.10** was investigated, and each polymerisation carried out using the *thermal method* or the *base method*. This would establish any thermal differences for polymers prepared using either linear and bent polymer networks and base and thermal promoted polymerisations.

As in previous chapters a nomenclature system will be adopted so that the reader can more easily identify the monomers and polymers being described in the text. For the dialkyne monomers which are amides **5.11-5.14** the oil of origin will be highlighted. (DAOA = oleic **5.11**, DALA = linoleic **5.12**, DARSA = rapeseed derived **5.13**, DASBA = soybean derived **5.14**), while the polyalkynated derivative from soybean oil **3.1** will be abbreviated to PASBO **3.1**. Polymers produced using base catalysis or *via* heating (thermal) will be given the abbreviation P^B and P^T respectively. While nitrile oxide monomer used to prepare the polymer (either **5.1** or **5.10**) will be identified with a subscripted META or PARA respectively. For example, P^T_{META}(DAOA) would refer to the polymer produced thermally from the *meta* nitrile oxide precursor **5.1** and the dialkynated oleamide **5.11**.

5.3 Synthesis of dialkyne monomers 5.11-5.14

Oleic derived, DAOA **5.11** and linoleic derived, DALA **5.12** were synthesised in a two step process from the corresponding acids using the mixed anhydride route described in chapter 4 (pgs 127 – 128). Hence, reaction of the corresponding acids with diethanolamine and ethyl chloroformate, initially at 0 °C for 30 minutes increasing to RT after removal of the hydrochloride by-product, gave oleamide

(DEtOA **4.11**) and linoleamide (DEtLA **4.11**) in 79 % and 91 % yield respectively. Alkynation of these diethanolamides, DEtOA **4.11** and DEtLA **4.11**, was achieved using sodium hydride and propargyl bromide in THF at room temperature to afford DAOA **5.11** and DALA **5.12** in 59 % and 60 % yields respectively (Scheme 5.5).

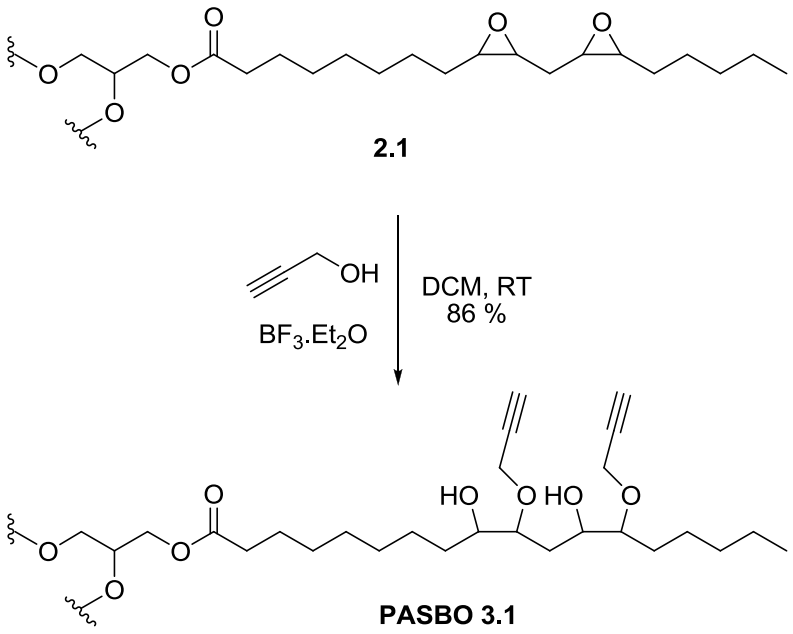


Scheme 5.5: Synthesis of DAOA 5.11 from oleic acid.

Triglyceride based analogues of **5.13** and **5.14** were synthesised using the same reaction procedures to give DARSA **5.13** and DASBA **5.14** in 61 % and 62 % yield respectively.

5.4 Synthesis of polyalkynated soybean oil monomer PASBO 3.1

The number of double bonds available in soybean oil is on average 4.6 as determined by iodine value calculations. This as it stands would prove an ideal candidate as a monomer for an alkene nitrile oxide based polymerisation to give a polyisoxazoline, however terminal alkenes and alkynes are more reactive than internal ones. We therefore decided to prepare the alkyne PASBO **3.1** from epoxidised soybean oil **2.1** (Scheme 5.6).

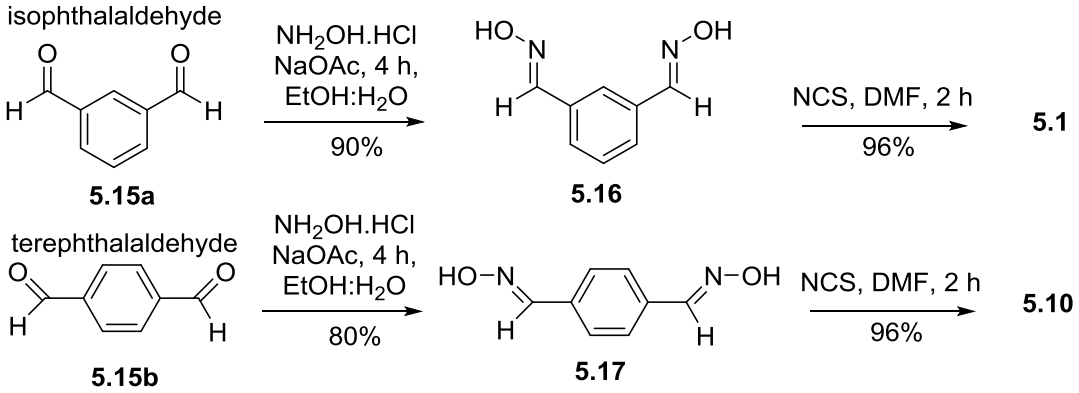


Scheme 5.6: Ring-opening of epoxidised soybean oil with propargyl alcohol.

Soybean oil was epoxidised using the Amberlite® method to give epoxidised soybean oil **2.1** in 90 % yield.[93] Subsequent ring opening was achieved using propargyl alcohol and $BF_3.OEt_2$ in DCM at room temperature. The reaction was complete in 10 minutes and afforded PASBO **3.1** in 86 % yield after purification though a silica plug.

5.5 Synthesis of nitrile-oxide precursors 5.1 and 5.10.

The nitrile oxides used in this study are prepared *in situ* by either base or heat mediated elimination of HCl from hydroximoyl dichlorides **5.1** and **5.10**. Due to the limited availability of suitable dialdehydes, which are the required precursors for hydroximoyl dichlorides, and for comparison with the work by Takata *et al*.[153-154] **5.1** and **5.10** from isophthalaldehyde **5.15a** and terephthalaldehyde **5.15b** respectively (Scheme 5.7) were prepared.



Scheme 5.7: Isophthalaldehyde 5.15a and terephthalaldehyde 5.15b.

Dialdehydes **5.15a-b** were reacted with hydroxylamine hydrochloride and sodium acetate in ethanol: water (1:1) for 4 hours and afforded dioxime **5.16** and **5.17** in 90 % and 80 % yields respectively. Subsequent reaction of **5.16** and **5.17** with *N*-chlorosuccinimide in DMF for 2 hours furnished isophthalohydroximoyl dichloride **5.1** and terephthalohydroximoyl dichloride **5.10** in 92 % and 96 % yields respectively.

5.6 Thermal analysis of alkyne monomers DAOA 5.11, DALA 5.12, DARSA 5.13, DASBA 5.14, PASBO 3.1, and nitrile oxide precursors 5.1 and 5.10.

Monomer	T_g (°C)[a]	T_{10} (°C)[a]	T_{50} (°C)[a]	T_{max} (°C)[a]
DAOA **5.11**	-75	350	418	501
DALA **5.12**	-80	350	423	506
DARSA **5.13**	-72	281	399	488
DASBA **5.14**	-63	243	386	490
PASBO **3.1**	-37	358	409	505

[a] Scan rate for DSC and TGA measured using 10 ºC/min.

Table 5.1: Thermal analysis of monomers 5.11-5.14 and 3.1.

DSC analysis of the monomers **5.11 – 5.14** and **3.1** shows various exotherms, the initial being due to the glass transition temperatures, the other exotherms are potentially due to liquid crystal transition phases as related diethanolamine fatty amides such as DEtOA **4.11** have been shown to have liquid crystal properties with smectic-isotropic melting temperatures between -46 °C and 40 °C (Fig. 5.3).[214-215] As expected the glass transition temperatures (T_g) for DAOA **5.11** and DALA **5.12** parallel the level of unsaturation in the monomer side-chains. Thus, the linoleic derivative DALA **5.12** with a higher unsaturation has a lower T_g (T_g = -80 °C) than for the oleic derivative DAOA **5.11** (T_g = -75 °C, ΔT_g = -5 °C). Conversely, an increase in the saturated fatty acid content increases the T_g, compare DAOA **5.11** (saturated fatty acid = 0%, T_g = -75 °C) with DARSA **5.13** (saturated fatty acid = 7%, T_g = -72 °C) and DASBA **5.14** (saturated fatty acid = 17%, T_g = -63 °C). The triglyceride derivative PASBO **3.1** has the highest T_g = -37 °C as expected (Table 5.1).

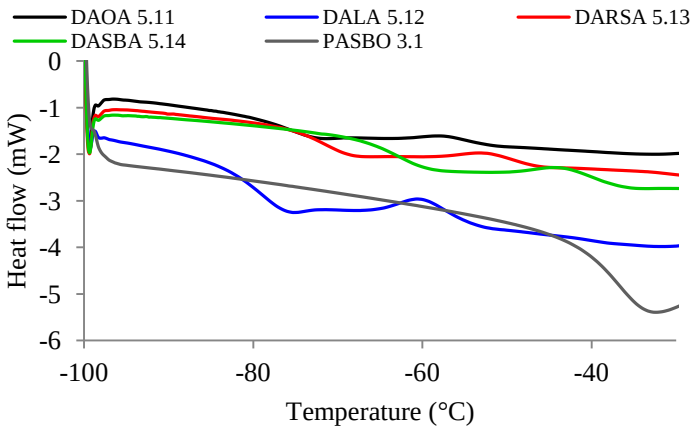


Figure 5.3: DSC of DAOA 5.11, DALA 5.12, DARSA 5.13, DASBA 5.14 and PASBO 3.1.

Hydrolysised triglyceride based monomers show a lower thermal stability caused by fatty acid present in the monomer (DARSA **3.13** = 20 %, DASBA **3.14** = 30 %) (Fig. 5.4).

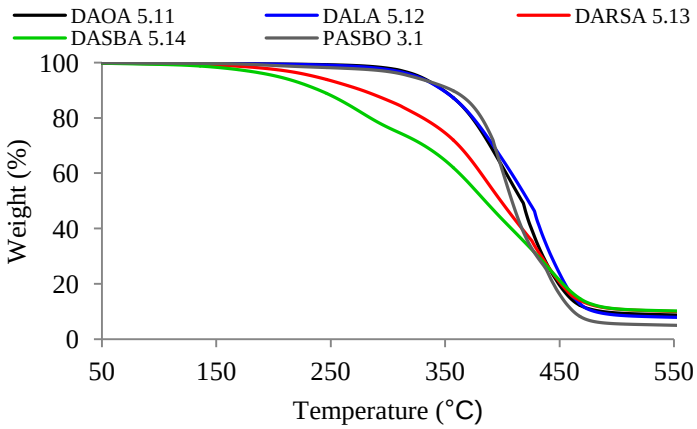


Figure 5.4: TGA of DAOA 5.11, DALA 5.12, DARSA 5.13, DASBA 5.14 and PASBO 3.1.

The thermal stability of the two hydroximoyl dichlorides **5.1** and **5.10** were next investigated, (Table 5.2). Initial decomposition starts to occur at 110 °C for **5.1** and at 115 °C for **5.10** and leads to 26% and 28% weight loss respectively (Fig. 5.5) by

170 °C. This decomposition pathway was assigned as being due to elimination of HCl to furnish nitrile oxides and suggested that carrying out a thermal reaction at these temperatures would be appropriate. T_g's could not be detected between -100 °C and 150 °C.

Nitrile oxide precursor	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
Meta **5.1**	172	337	585
Para **5.10**	181	360	582

[a] Scan rate for TGA measured using 10 ºC/min.

Table 5.2: Thermal analysis of 5.1 and 5.10.

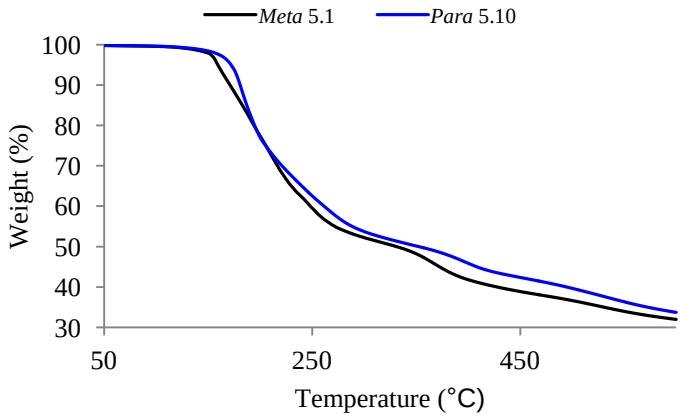
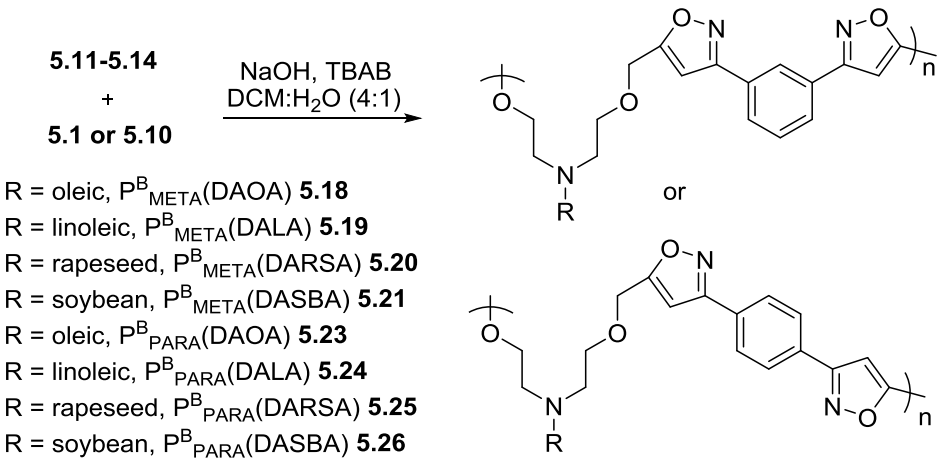


Figure 5.5: TGA of 5.1 and 5.10.

5.7 Base promoted polymerisation of fatty amide monomers 5.11-5.14 and triglyceride monomer 3.1 with dihydroxymoyl dichlorides 5.1 and 5.10

Polymerisations were attempted in two ways, either *via* a base promoted protocol (P^B) or a thermal approach (P^T). The first approach was the base promoted method. We chose to use the same conditions as Takata *et al*. using equal equivalents of both

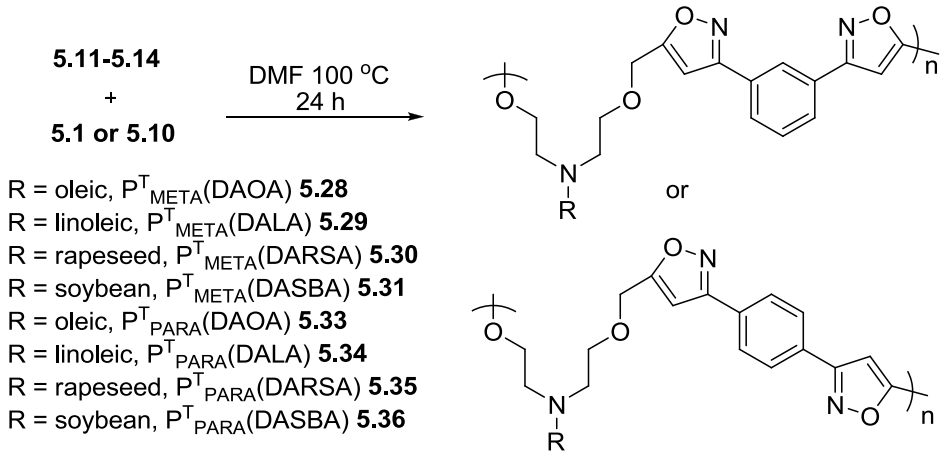
alkyne monomers **5.11 – 5.14** and dihydroxymoyl dichloride **5.1** or **5.10**, with NaOH in DCM: H_2O (4:1) as base and 5 mol% of tetra-*n*-butylammonium bromide as a phase transfer catalyst at room temperature for 24 hours (Scheme 5.8). The stoichiometry of reaction with PASBO **3.1** was altered to reflect the different number of reactive alkyne groups giving P^B_{META}(PASBO) **5.22** and P^B_{PARA}(PASBO) **5.27**.



Scheme 5.8: Base promoted polymerisations.

A disadvantage of this polymerisation method is that NaBr becomes trapped within the polymer network which is likely to effect the material properties of the polymers and make rationalisation of trends difficult, consequently, the second approach to polymerisation was a modification of the thermal method by Takata *et al*.[153] As both **5.1** and **5.10** were solids at RT a non-volatile solvent, in which **5.1** and **5.10** were soluble (DMF, toluene or acetone), was required. The higher boiling point of DMF made it ideal and ensured the reagents remained homogenous during the polymerisation. Takata's original work was carried out at 100 °C, and even though our thermal studies indicated that nitrile oxide formation occurred between 100-200 °C the lower temperature was chosen (Scheme 5.9). Hence, heating the monomers in a small amount of DMF for 24 hours at 100 °C both followed by evaporation of any

residual solvent furnished polymers P^T(**5.28 – 5.36**). As before the stoichiometry of reaction with PASBO **3.1** was altered to reflect the different number of reactive alkyne groups giving P^T_{META}(PASBO) **5.32** and P^T_{PARA}(PASBO) **5.37** .



Scheme 5.9: Thermally promoted polymerisations.

Polymerisation with **5.1** using either the base or thermal method led to P^B_{META}(**5.18 – 5.21**) and P^T_{META}(**5.28 – 5.31**) organic soluble polymers but reactions with the linear nitrile oxide precursor **5.10** or PASBO **3.1** produced insoluble materials. For the organic soluble materials P^B_{META}(**5.18-5.21**) and P^T_{META}(**5.28-5.31**), polymerisation could be confirmed by both ^{1}H NMR (chloroform) and GPC. The 300 MHz ^{1}H NMR spectrum of P^B_{META}(DAOA) **5.18** and P^T_{META}(DAOA) **5.28**, (Fig. 5.6) shows broadening of peaks and the 3,5-disubstituted isoxazole ring could be positively identified. The peaks at 6.63 ppm in both spectra are indicative for the proton shift for the hydrogen in the 3,5-disubstituted isoxazole ring while the peak at 4.64 ppm is characteristic for the CH_2 group attached to the isoxazole group. No peak at 8.47 ppm representative of a 3,4-disubstituted isoxazole was observed highlighting the cycloaddition was highly regioselective in both cases. There is a small peak at 3.30 ppm in both spectra, which is tentatively assigned as an isoxazoline formed by

cycloaddition to the *cis* double bonds present in the side-chains. Further evidence for this is that the integrals for the alkene protons at 5.34 ppm relative to the methyl groups at 0.88 ppm are lower for P^{B}_{META}(DAOA) **5.18** (3.07 : 6.00) and P^{T}_{META}(DAOA) **5.28** (3.09 : 6.00) than in the monomer **5.11** (3.98 : 6.00).

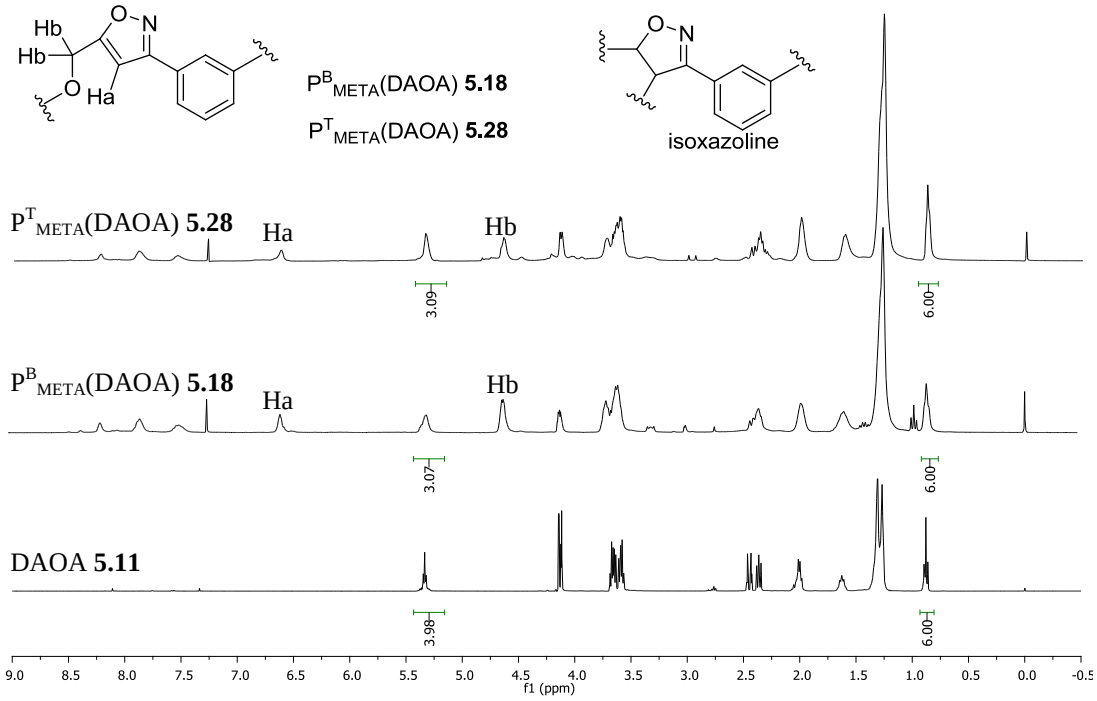


Figure 5.6: 300MHz ^{1}H NMR spectrum of 5.11, P^{B}_{META}(DAOA) 5.18 and P^{T}_{META}(DAOA) 5.28.

The MWt of the polymers P^{B}_{META}(**5.18**-**5.21**) and P^{T}_{META}(**5.28**-**5.31**) were all higher than those of Takata *et al*. (P^{B}_{META}(DAOA) **5.18** M_w *= 4600 vs polyisoxazole* ***5.7*** *Mw = 1900*). However, the thermal method in the main gives slightly lower molecular weight polymers with marginally higher PD's (Table 5.3).

Polymer	M_n[a]	M_w[a]	PD[a]
P^B_{META}(DAOA) **5.18**	1900	4600	2.37
P^B_{META}(DALA) **5.19**	1600	4500	2.72
P^B_{META}(DARSA) **5.20**	1100	2600	2.35
P^B_{META}(DASBA) **5.21**	1100	2400	2.13
P^T_{META}(DAOA) **5.28**	1400	3800	2.68
P^T_{META}(DALA) **5.29**	1300	4400	3.28
P^T_{META}(DARSA) **5.30**	1300	3100	2.47
P^T_{META}(DASBA) **5.31**	1000	2200	2.14

[a] Estimated by GPC based on polystyrene standards

Table 5.3: GPC analysis of soluble polymers.

The molecular weights for the polymers prepared from hydrolysed triglycerides DARSA **5.13** or DASBA **5.14** generally show a lower M_w than those prepared from the fatty acids DAOA **5.11** and DALA **5.12**. Although the thermal approach provide materials with lower M_w's and higher PD's it can be accomplished without the need for molecular sieves, which means, samples could potentially be prepared for mechanical testing in future. Further work is required to optimise this process as HCl is evolved in the polymerisation and can become trapped within the polymer network creating large air pockets which would lead to weakness in the polymers and errors in mechanical properties.

5.8. Thermal analysis of P^B_{META}(5.18-5.22) P^B_{PARA}(5.23-5.27), P^T_{META}(5.28-5.32) and P^T_{PARA}(5.33-5.37).

In general, *meta* polymers have a lower T_g than their *para* derivatives irrespective of their method of synthesis, (e.g. for the oleic acid series: P^B_{META}(DAOA) **5.18** T_g = -20 °C < P^B_{PARA}(DAOA) **5.23** T_g = -9 °C and P^T_{META}(DAOA) **5.28** T_g = -28 °C < P^T_{PARA}(DAOA) **5.33** T_g = 1 °C) (Table 5.4). This is presumably due to more efficient

packing for the *para* derived polymers compared to the *meta* derived ones. T_g's of all of the polymers are lower than those reported by Takata *et al*. which is to be expected due to the large aliphatic side groups present in P(**5.18**-**5.37**). It is interesting to note that within each series P^B_{META}, P^B_{PARA}, P^T_{META} and P^T_{PARA} the T_g's for DARSA and DASBA derivatives are similar and the polymers produced from PASBO **3.1** show the highest T_g irrespective of their method of preparation, (P^B_{META}(PASBO) **5.22** T_g = 10 °C, P^B_{PARA}(PASBO) **5.27** T_g = 18 °C, P^T_{META}(PASBO) **5.32** T_g = 0 °C, P^T_{PARA}(PASBO) **5.37** T_g = 11 °C). This latter observation is due to the increased ability to cross-link in the PASBO **3.1** derived materials.

Polymer	T_g (°C)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
P^B_{META}(DAOA) **5.18**	-20	316	423	590
P^B_{META}(DALA) **5.19**	-9	308	453	597
P^B_{META}(DARSA) **5.20**	-22	304	451	590
P^B_{META}(DASBA) **5.21**	-23	302	449	570
P^B_{META}(PASBO) **5.22**	10	357	422	581
P^B_{PARA}(DAOA) **5.23**	-9	310	455	593
P^B_{PARA}(DALA) **5.24**	-28	322	446	568
P^B_{PARA}(DARSA) **5.25**	-14	292	444	581
P^B_{PARA}(DASBA) **5.26**	-10	282	456	562
P^B_{PARA}(PASBO) **5.27**	18	322	424	580
P^T_{META}(DAOA) **5.28**	-28	308	384	598
P^T_{META}(DALA) **5.29**	-15	303	417	578
P^T_{META}(DARSA) **5.30**	-23	296	392	577
P^T_{META}(DASBA) **5.31**	-20	297	419	571
P^T_{META}(PASBO) **5.32**	0	325	409	580
P^T_{PARA}(DAOA) **5.33**	1	263	386	568
P^T_{PARA}(DALA) **5.34**	7	272	435	583
P^T_{PARA}(DARSA) **5.35**	-5	257	400	556
P^T_{PARA}(DASBA) **5.36**	-2	249	423	588
P^T_{PARA}(PASBO) **5.37**	11	249	403	563

[a] Scan rate for DSC and TGA measured using 10 ºC/min.

Table 5.4: Thermal analysis of polymers prepared by base and thermal processes.

The method of preparation of the polymers is important in determining their properties with significant differences arising between materials prepared thermally or *via* the use of a base. The biggest differences seem to be for the *para* derived polymers. This highlights that encapsulation of NaBr and the phase transfer catalyst into the polymeric materials is affecting their properties.

Meta based polymers P^{B}_{META} (**5.18** – **5.22**) generally have a higher initial degradation T_{10} than the para derivatives P^{B}_{PARA} (**5.23** – **5.27**) (Fig. 5.7), this difference is more marked in the thermally derived materials P^{T}_{META} (**5.28** – **5.32**) vs P^{T}_{PARA} (**5.33** – **5.37**). All polymers with para linkers (prepared using the base approach), show three-step degradations while only two of the meta series P^{B}_{META}(DAOA) **5.18** and P^{B}_{META}(DALA) **5.19** show a similar profile, (appendix 4). This extra degradation step could be due to unreacted monomers isophthalohydroximoyl dichloride **5.1** and terephthalohydroximoyl dichloride **5.10** undergoing decomposition, as the degradation is observed around 170 °C and is consistent with that observed for pure monomer, (Fig. 5.5).

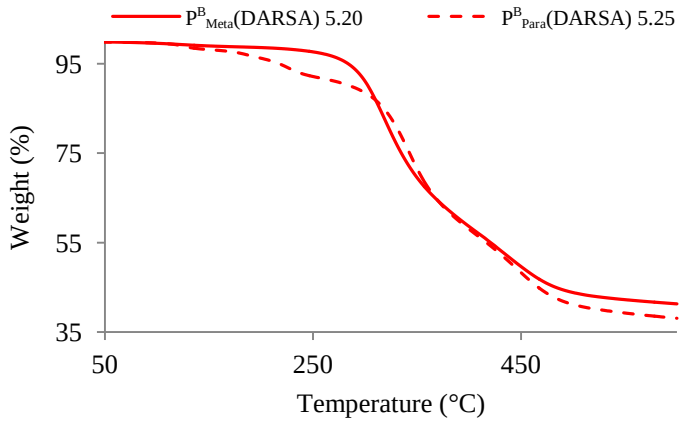


Figure 5.7: TGA of P^{B}_{META}(DARSA) 5.20 and P^{B}_{PARA}(DARSA) 5.25 showing three-step degradation for para derived material.

Three-step degradation is not observed for polymers produced *via* the thermal approach, indicating that this method ensures complete consumption of **5.1** and **5.10** (Fig. 5.8a). Both polymers made with alkynated soybean oil (PSBO **3.1**) show a small degradation around 420 °C however again with the para polymer there is an initial degradation around the terephthalohydroximoyl chloride (**5.8**) degradation temperature (170 °C) (appendix 4).

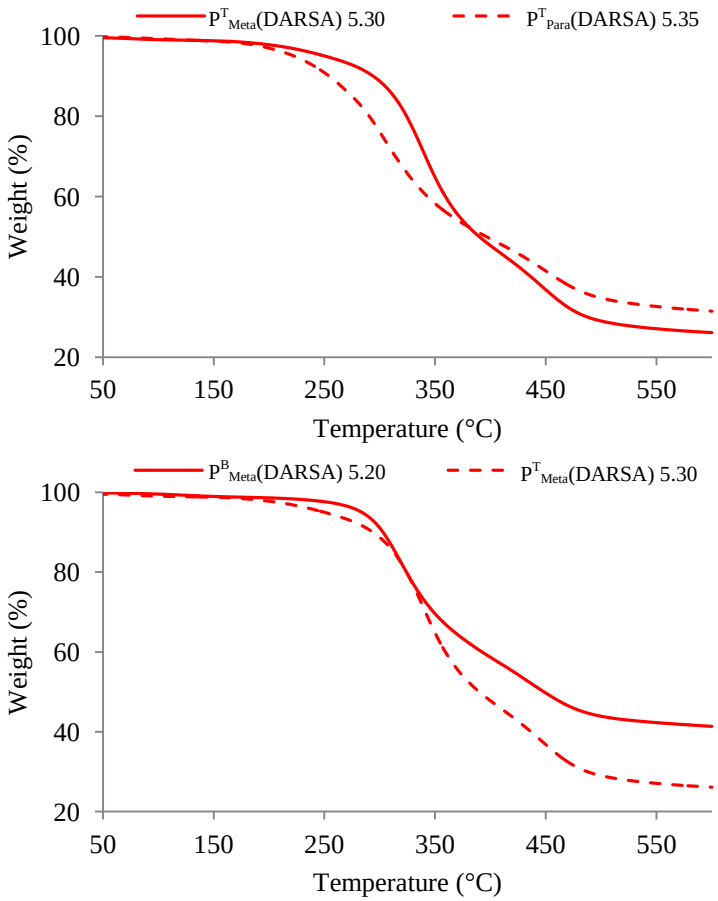


Figure 5.8: a) TGA of P^{T}_{META}(DARSA) 5.30 and P^{T}_{PARA}(DARSA) 5.35, b) TGA of P^{B}_{META}(DARSA) 5.20 and P^{T}_{META}(DARSA) 5.30.

In general, *meta* based polymers P^{T}_{META} (**5.28 – 5.32**) have a higher thermal stability compared to their *para* based analogues P^{T}_{PARA} (**5.28 – 5.32**), (Fig. 5.8b) and for the *meta* series, base prepared polymers, e.g. P^{B}_{META}(DARSA) **5.20** have a marginally

higher stability than thermally prepared ones, P^{T}_{META}(DARSA) **5.30** (Fig. 5.8b), this is potentially due to the NaBr trapped in the polymer network however further studies are required to fully establish the cause of this effect.

5.9 Summary and Conclusion

Low molecular weight nitrile-oxide 'click' polymers were synthesised from functionalised fatty acids and dihydroxymoyl dichlorides *via* base or thermal promoted methods. Molecular weights were low and the *meta* series were soluble in organic solvents. Thermally prepared polymers had slightly lower molecular weights than the base promoted series (P^{B}_{META}(DAOA) **5.18** M_w = *4600*, P^{T}_{META}(DAOA) **5.28** M_w = *3800*) which compared well with those synthesised by Takata *et al.* (*polyisoxazole* ***5.7*** M_w = *1900*). Unlike, Takata's work, molecular sieves were not required, and this would reduce the cost of large scale polymerisations and also allow potential production of samples suitable for mechanical testing.

Incorporation of a bend in the polymer network causes a decrease in glass transition temperatures (P^{B}_{META}(DAOA) **5.18** T_g = *-20 °C*, P^{B}_{PARA}(DAOA) **5.18** T_g = *-9 °C*, ΔT_g = *-11 °C*) as expected due to better packing in linear polymer chains

Polymers derived from the muli-alkyne functional monomer PASBO **3.1** all had higher glass transition temperatures caused by an increased amount of cross-linking. As before *para* derivatives gave higher T_g's than *meta* derivatives (P^{B}_{META}(PASBO) **5.22** T_g = *10 °C*, P^{B}_{PARA}(PASBO) **5.27** T_g = *18 °C*, ΔT_g = *+8 °C*) and base mediated

materials gave higher T_g's than thermally derived polymers (P^B_{META}(PASBO) **5.22** *T_g = 10 °C*, P^T_{META}(PASBO) **5.32** *T_g = 0 °C, ΔT_g = -10 °C*).

5.10 Future work

When alkene and alkyne functional groups are both present in the monomers, terminal alkynes have been shown to react preferentially over disubstituted alkenes, as expected. More in depth thermal analysis of nitrile oxide-alkene polymerisations using alkene derivatives would allow the comparison of properties of polyisoxazoles with polyisoxazolines.

Reduction of polyisoxazoles with $LiAlH_4$ would give rise to renewable poly(b-aminoalcohols) which could undergo cross-linking with dialdehydes or via diisocyanates to produce materials with potential as ion exchange resins or ion channels.

The effect of the level of alkyne functionality on the properties of materials prepared from other triglyceride oil derivatives other than soybean PASBO **3.1** such as linseed, rapeseed and castor oil would allow a range of materials with different properties to be prepared and exploited.

6.0 Experimental

6.1 General procedures and Information

The starting materials used in the synthesis were obtained from commercial suppliers and used as received without any further purification. Drysyn© apparatus was used to achieve heat transfer during the synthesis of the monomers, silicone moulds and conventional oven for the click polymerisations and for polyurethane curing.

TLC was carried out using Merck silica gel coated aluminium sheets as the stationary phase (Merck Kieselgel $60F_{254}$ 230-400 mesh). The TLC plate was visualised using UV lamp (254 nm) and stained using potassium permanganate solution. Flash column chromatography was carried out using ZEOprep 60 SiO_2 (200-425 mesh).

^{1}H and ^{13}C NMR were performed on a Bruker DPX-400 spectrometer, at 400 MHz and 100 MHz respectively. All chemical shifts were in parts per million (ppm) relative to the tetramethylsilane (TMS) internal standard (0.03 % v/v, 0.00 ppm). Coupling constants (*J*) were expressed in Hertz (Hz).

Infrared spectra were recorded on a Bruker ALPHA platinum ATR Fourier Transform spectrometer. Absorptions were recorded in wavenumbers (cm^{-1}). Mass spectrometry was achieved using an Agilent 6130B single Quad (ESI).

GPC was performed on an Agilent 390-MDS with autosampler using a PLgel 5.0 µm bead-size guard column (50 x 7.5 mm), followed by two linear 5.0 µm bead-size PLgel Mixed D columns (300 x 7.5 mm) and a differential refractive index detector. Using $CHCl_3$ as eluent the system was calibrated using linear poly(styrene) EasiVial

standards (Agilent Ltd.) range from 162 to $5x10^5$ Da. Data was collected and analysed using Cirrus GPC/SEC (version 3.3) and Agilent GPC/SEC software.

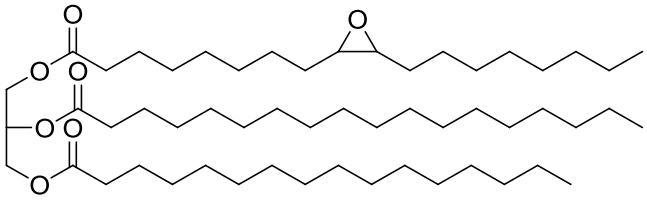
TGA, DSC and melting points were carried out using Metler Toledo DSC1-Star with 40 µl standard aluminium pans and autosampler. Samples heated from -100 – 70 °C, cooled to -100 and heated from -100 – 600 °C under N_2 atmosphere for DSC and heated from 25 – 600 °C for TGA. T_g values determined were midpoints of the transitions.

Fatty acid composition by gas chromatography was carried out by Warwick HRI.

The following compounds were synthesised using oils and so contain mixtures of fatty acids. The names of the compounds reflect the structures drawn however the analysis is of a number of products. Cocoa butter derived products are denoted by stearic chains, rapeseed oil with oleic chains and soybean oil with linoleic chains. Oleic acid (95 %) and linoleic acid (60 %) derived products are analysed as oleic and linoleic chains respectively.

6.2 General procedures in chapter 2

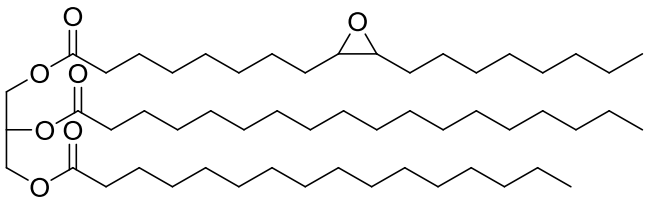
6.2.1 Synthesis of epoxidised cocoa butter using Venturello's catalyst (2.11)



Tungsten catalyst was prepared using tungsten powder (0.6 g, 3 mol, 0.025 equiv.), hydrogen peroxide (8 mL, 93 mmol, 0.8 equiv.), water (4 mL, 0.8 M), and heated at 60 °C until tungsten powder had completely dissolved. Orthophosphoric acid (0.4 g, 4 mmol, 0.035 equiv.) and water (4 ml) was added to catalyst when cooled. Cocoa

butter (100 g, 116 mmol, 1.0 equiv.) and Adogen 464 (0.8 g, 2 mmol, 0.02 equiv.) were heated to 60 °C when the catalyst, hydrogen peroxide (120 ml, 1.4 mol, 12.0 equiv.) and water (160 mL, 0.7 M) were added and left to react with stirring for 4 hours. Reaction was then cooled and extracted with $CHCl_3$. The organic layer was washed with water (2 x 250 mL) then saturated NaCl (250 mL) followed by drying over $MgSO_4$ and solvent removed *in vacuo* to give pure product as cream solid (99 %).; ν_{max} / cm^{-1}: 2914 (C-H) , 1729 (C=O), 1209 (epoxide C-H).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (p, *J* = 4.9 Hz, 1H, $OCH_2CH(O)CH_2O$), 4.22 (ddd, *J* = 17.8, 11.9, 5.0 Hz, 4H, $OCH_2CH(O)CH_2O$), 3.00 – 2.82 (m, 2H, $HC(O)CH$), 2.31 (t, *J* = 7.5 Hz, 6H, $O=CCH_2CH_2$), 1.65 – 1.56 (m, 6H, $O=CCH_2CH_2$), 1.51 – 1.46 (m, 4H, $CH_2CH(O)CHCH_2$), 1.46 – 1.15 (m, 72H, CH_2), 0.88 (t, *J* = 6.5 Hz, 9H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.37 ($O=CCH_2CH_2$), 172.89 ($O=CCH_2CH_2$), 69.01 ($OCH_2CH(O)CH_2O$), 62.17 ($OCH_2CH(O)CH_2O$), 57.31 ($HC(O)CH$), 57.25 ($HC(O)CH$), 34.25 ($O=CCH_2CH_2$), 34.14 ($O=CCH_2CH_2$), 32.03 (CH_2), 31.96 (CH_2), 29.80 (CH_2), 29.77 (CH_2), 29.73 (CH_2), 29.65 (CH_2), 29.58 (CH_2), 29.47 (CH_2), 29.38 (CH_2), 29.33 (CH_2), 29.22 ($CH_2CH(O)CHCH_2$), 29.07 (CH_2), 27.94 (CH_2), 26.72 (CH_2), 24.96 ($O=CCH_2CH_2$), 24.93 (CH_2), 22.79 (CH_2), 14.21 (CH_3).; *ms* (ES+) 889.6 $[M+Na]^+$

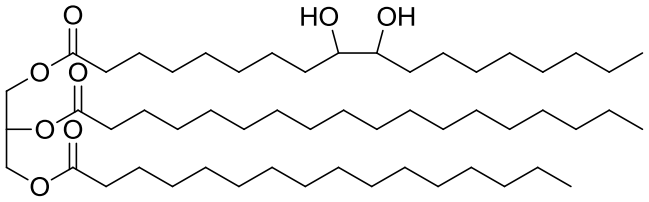
6.2.2 Synthesis of epoxidised cocoa butter using Amberlite® method (2.11)



Cocoa butter **2.9** (200 g, 230 mmol, 1.0 equiv.) was dissolved in toluene (300 mL, 0.7 M) and heated at 80 °C. Amberlite (50 g, 25 wt%) and acetic acid (6.9 g, 115

mmol, 0.5 equiv.) was added followed by hydrogen peroxide (45 mL, 460 mmol, 2 equiv.) dropwise. After complete addition of hydrogen peroxide the reaction was left stirring for 8 hours at 80 °C. The reaction was cooled and further diluted with toluene then the Amberlite was filtered off. The organic layer was washed with water (2 x 500 mL) followed by saturated NaCl (500 mL) followed by drying over $MgSO_4$ and finally solvent removed *in vacuo* to give pure product as a cream solid (88 %)

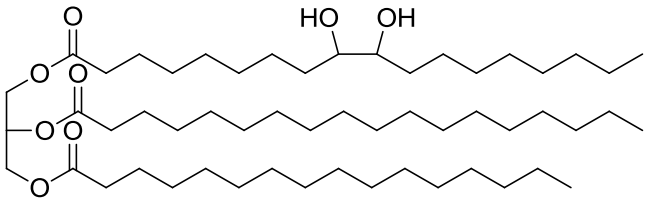
6.2.3 Synthesis of ring opening of Cocoa butter (2.10(0%))



Cocoa butter (5 g, 5.7 mmol, 1.0 equiv.) and water (5.7 mL, 1 M) was heated to 100 °C. Adogen 464 (0.012 g, 2.5 wt%) was added followed by orthophosphoric acid (0.56 g, 5.7 mmol, 1.0 equiv). The reaction was heated at 100 °C for 24 h. The reaction was extracted with Et_2O, washed with water (2 x 10 mL) followed by saturated NaCl (10 mL). Organic layer was dried over $MgSO_4$ and solvent removed *in vacuo* to give pure product (97 %). ν_{max} / cm^{-1}: 3341 (O-H), 2915 (C-H), 1736 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (p, *J* = 5.3 Hz, 1H, $OCH_2CH(O)CH_2O$), 4.22 (ddd, *J* = 17.6, 11.9, 4.8 Hz, 4H, $OCH_2CH(O)CH_2O$), 3.64 – 3.32 (m, 4H, $CH_2CH(OH)$, OH), 2.31 (t, *J* = 7.4 Hz, 6H, $O=CCH_2CH_2$), 1.64 – 1.56 (m, 6H, $O=CCH_2CH_2$), 1.53 – 1.43 (m, 4H, $CH_2CH(OH)$), 1.37 – 1.23 (m, 70H, CH_2), 0.88 (t, *J* = 6.3 Hz, 9H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.44 ($O=CCH_2CH_2$), 172.95 ($O=CCH_2CH_2$), 74.64 ($CH_2CH(OH)$), 74.57 ($CH_2CH(OH)$), 68.99 ($OCH_2CH(O)CH_2O$), 62.16 ($OCH_2CH(O)CH_2O$), 34.23 ($O=CCH_2CH_2$), 34.14

(O=C*C*H_2CH_2), 33.70 (*C*H_2CH(OH)), 33.64 (*C*H_2CH(OH)), 32.02 (C*H*$_2$), 31.98 (C*H*$_2$), 29.79 (C*H*$_2$), 29.76 (C*H*$_2$), 29.58 (C*H*$_2$), 29.46 (C*H*$_2$), 29.37 (C*H*$_2$), 29.21 (C*H*$_2$), 29.03 (C*H*$_2$), 25.79 (O=*C*CH_2CH_2), 25.68 (O=CCH_2*C*H_2), 24.95 (C*H*$_2$), 24.90 (C*H*$_2$), 22.78 (C*H*$_2$), 14.20 (C*H*$_3$).; *ms* (ES+) 917.8 $[M+Na]^+$

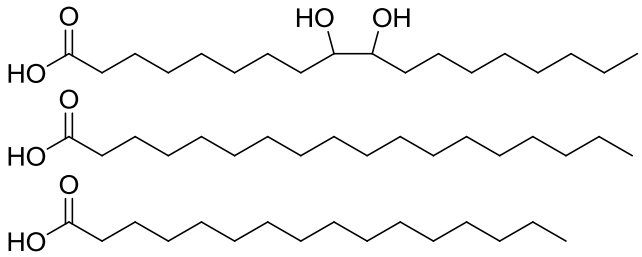
6.2.4 Hydroxylation of Cocoa butter (2. 10(25%))



The catalyst was prepared using tungsten powder (16.2 g, 0.88 mol), hydrogen peroxide (120 ml, 3.91 mol), water (60.0 ml) and heated at 60 °C with stirring until the tungsten powder had completely dissolved. Orthophosphoric acid (16.2 g, 0.16 mol) and water (120 ml) was added to catalyst when cooled. Cocoa butter (3.00 kg, 3.44 mol) and Adogen 464 (21.1 g, 0.05 mol) was heated to 60 °C. Catalyst, hydrogen peroxide (700 ml, 22.8 mol) and water (4920 ml) was then added and temperature increased to 100 °C and left with stirring for 24 hours. The reaction was diluted with $CHCl_3$. The organic layer was washed with water (2 x 1000 mL) then saturated NaCl (500 mL) followed by drying over $MgSO_4$ and finally the solvent was removed *in vacuo* to give pure product as cream solid (99 %).; ν_{max} / cm^{-1}: 3341 (O-H), 2914 (C-H), 2847 (C-H), 1697 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 – 5.31 (br s, 2H, O*H*), 5.30 – 5.18 (m, 1H, OCH_2C*H*(O)CH_2O), 4.30 (dd, *J* = 11.9, 3.7 Hz, 1H OC*H*$_2$CH(O)C*H*$_2$O triglyceride), 4.20 – 4.05 (m, 3H, OC*H*$_2$CH(O)C*H*$_2$O triglyceride, diglyceride), 3.74 – 3.32 (m, 2H, CH_2C*H*(OH)), 2.38 – 2.27 (m, 6H, O=CC*H*$_2$CH$_2$)), 1.68 – 1.56 (m, 6H, O=CCH$_2$C*H*$_2$)), 1.52 – 1.40 (m, 4H, C*H*$_2$CH(OH)), 1.38 – 1.15 (m, 70H, C*H*$_2$), 0.88 (t, *J* = 6.3 Hz, 9H, C*H*$_3$).; ^{13}C NMR

(101 MHz, $CDCl_3$) δ 179.06 (O=*C*CH_2CH_2 fatty acid), 174.05 (O=*C*CH_2CH_2), 173.46 (O=*C*CH_2CH_2), 172.97 (O=*C*CH_2CH_2), 74.68 (CH_2*C*H(OH)), 74.61 (CH_2*C*H(OH)), 72.62 (CH_2*C*H(OH)), 72.18 (CH_2*C*H(OH)), 70.34 (OCH_2*C*H(O)CH_2O), 68.99 (CH_2*C*H(OH)), 68.26 (CH_2*C*H(OH)), 68.22 (CH_2*C*H(OH)), 65.06 (O*C*H_2CH(O)*C*H_2O), 63.43 (O*C*H_2CH(O)*C*H_2O), 62.16 (O*C*H_2CH(O)*C*H_2O), 34.60 (O=C*C*H_2CH_2 fatty acid), 34.49 (O=C*C*H_2CH_2 fatty acid), 34.18 (O=C*C*H_2CH_2), 34.12 (O=C*C*H_2CH_2), 33.58 (*C*H_2CH(OH)), 33.47 (*C*H_2CH(OH)), 32.01 (*C*H_2), 30.70 (*C*H_2), 29.78 (*C*H_2), 29.75 (*C*H_2), 29.55 (*C*H_2), 29.45 (*C*H_2), 29.35 (*C*H_2), 29.19 (*C*H_2), 29.09 (*C*H_2), 29.03 (*C*H_2), 28.94 (*C*H_2), 26.12 (*C*H_2), 25.76 (*C*H_2), 25.67 (*C*H_2), 25.53 (*C*H_2), 25.23 (*C*H_2), 24.94 (*C*H_2), 24.89 (*C*H_2), 24.83 (*C*H_2), 24.72 (O=CCH_2*C*H_2), 22.83 (*C*H_2), 22.77 (*C*H_2), 14.19 (*C*H_3). *ms* (ES+) 917.3 $[M+Na]^+$ (C18:1, C18:0, C16:0), 679.2 $[M+Na]^+$ (C18:1, C18:0), 651.2 $[M+Na]^+$ (C18:1, C16:0), 307.2 $[M+Na]^+$ (C18:0), 279.2 $[M+Na]^+$ (C16:0).

6.2.5 Ring-opening and hydrolysis of epoxidised cocoa butter (2. 10(100%))



Epoxidised cocoa butter (20 g, 23 mmol, 1.0 equiv.) and water (100 mL, 0.2M) was heated to 100 °C with stirring. NaOH (4.6 g, 114 mmol, 5.0 equiv.) was added and left to react at 100 °C overnight. The reaction mixture was acidified until pH 3 then cooled. The solid precipitate was dissolved in $CHCl_3$ and separated. Organic layer was washed with water (2 x 50 mL) followed by saturated NaCl (50 mL). The organic layer was dried over $MgSO_4$ and then the solvent was removed *in vacuo* to

give pure product (88 %).; ν_{max} / cm^{-1}: 3351 (O-H), 2914 (C-H), 2847 (C-H), 1698 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 – 3.02 (m, 2H, CH_2CH(OH)), 2.34 (t, *J* = 7.4 Hz, 6H, O=CCH_2CH_2), 1.66 – 1.59 (m, 6H, O=CCH_2CH_2), 1.52 – 1.38 (m, 4H, CH_2CH(OH)), 1.38 – 1.20 (m, 72H, CH_2), 0.88 (t, *J* = 6.3 Hz, 9H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.29 (O=CCH_2CH_2), 74.77 (CH_2CH(OH)), 74.71 (CH_2CH(OH)), 74.10 (CH_2CH(OH)), 74.06 (CH_2CH(OH)), 72.75 (CH_2CH(OH)), 69.05 (CH_2CH(OH)), 68.95 (CH_2CH(OH)), 34.24 (O=CCH_2CH_2), 32.07 (CH_2), 32.01 (CH_2), 29.83 (CH_2), 29.73 (CH_2), 29.64 (CH_2), 29.58 (CH_2), 29.50 (CH_2), 29.38 (CH_2), 29.21 (CH_2), 29.06 (CH_2), 24.82 (CH_2), 24.74 (CH_2), 22.82 (CH_2), 14.23 (CH_3).; *ms* (ES+) 339.2 $[M+Na]^+$ (C18:1), 307.2 $[M+Na]^+$ (C18:0), 279.2 $[M+Na]^+$ (C16:0).

6.2.6 General procedure for the synthesis of polyurethanes

Cocoa butter diol (1.0 equiv.) was added to a 50 ml round bottomed flask and was heated to 80 °C under vacuum with stirring. MDI (1.05 equiv) was added and returned to vacuum and left for 2 mins with minimal stirring. The mixture was poured into a mould and left in a 60 °C oven for 24 h until fully cured.

Synthesis of polyurethane (PU2.10(0%)): The general procedure for the synthesis of polyurethanes was applied using **2.10(0%)** (5.0 g, 5.6 mmol, 1.0 equiv.) and MDI (1.5 g, 5.9 mmol, 1.05 equiv.) to give a cream coloured polymer; ν_{max} / cm^{-1}: 2914 (C-H), 2871 (C-H), 1739 (C=O) 1727 (C=O).

Synthesis of polyurethane (PU2.10(25%)): The general procedure for the synthesis of polyurethanes was applied using **2.10(25%)** (5.0 g, 5.6 mmol, 1.0 equiv.) and MDI (1.5 g, 5.9 mmol, 1.05 equiv.) to give a cream coloured polymer; ν_{max} / cm^{-1}: 2954 (C-H), 2847 (C-H), 1697 (C=O).

Synthesis of polyurethane (PU2.10(100%)): The general procedure for the synthesis of polyurethanes was applied using **2.10(100%)** (5.0 g, 5.6 mmol, 1.0 equiv.) and MDI (1.5 g, 5.9 mmol, 1.05 equiv.) to give a cream coloured polymer; ν_{max} / cm^{-1}: 2914 (C-H), 2847 (C-H), 1698 (C=O).

6.2.7 General procedure for the synthesis of dyed polyurethanes

Cocoa butter diol (1.0 equiv.) was added to a 50 ml round bottomed flask and was heated to 80 °C under vacuum with stirring. Brilliant Blue FCF (0.002 equiv.) was added and stirred under vacuum for 10 mins. MDI (1.05 equiv) was added and returned to vacuum for 2 mins with minimal stirring. The mixture was poured into a mould and left in a 60 °C oven for 24 h until fully cured.

Synthesis of polyurethane (2.16PU2.10(0%)): The general procedure for the synthesis of dyed polyurethanes was applied using **2.10(0%)** (5.0 g, 5.6 mmol, 1.0 equiv.) and MDI (1.5 g, 5.9 mmol, 1.05 equiv.) to give a cream coloured polymer; ν_{max} / cm^{-1}: 2914 (C-H), 2847 (C-H), 1700 (C=O).

Synthesis of polyurethane (2.16PU2.10(25%)): The general procedure for the synthesis of dyed polyurethanes was applied using **2.10(25%)** (5.0 g, 5.6 mmol, 1.0 equiv.) and MDI (1.5 g, 5.9 mmol, 1.05 equiv.) to give a cream coloured polymer; ν_{max} / cm^{-1}: 2954 (C-H), 2847 (C-H), 1697 (C=O).

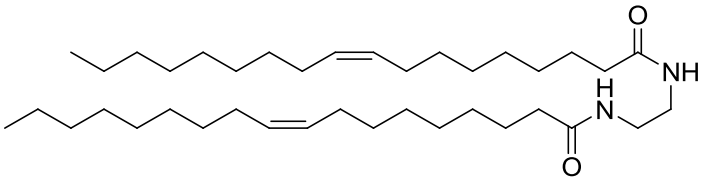
6.3 General Procedures in Chapter 3

6.3.1 General Procedure for the synthesis of difatty amides

The desired fatty acid or triglyceride (1 equiv.) was added to 100 mL round bottomed flask and heated to 150 °C. Diamine (0.5 equiv. for fatty acids, 1.5 equiv.

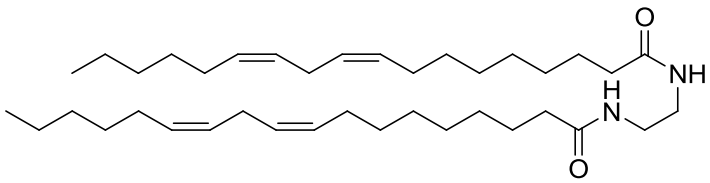
for triglycerides) was and the mixture was reacted overnight at 150 °C. The reaction mixture dissolved in acetone and the precipitate was filtered off and redissolved in chloroform. The chloroform layer was washed with 15 % NaCl and dried over $MgSO_4$, The solvent was removed in *vacuo.* to give pure product.

(*Z*)-*N*,*N'*-(ethane-1,2-diyl)dioleamide (3.20)



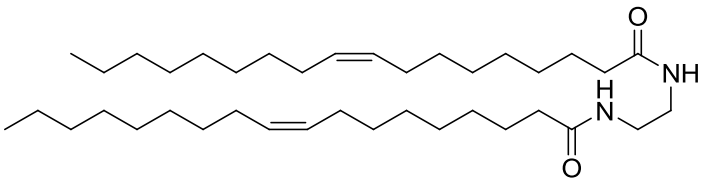
The general procedure for the synthesis of difatty amides was applied using oleic acid (20 g, 71 mmol, 1.0 equiv.), and ethylene diamine (2.36 mL, 35 mmol, 0.5 equiv.) to give the product as a white solid. (35 %); ν_{max}/cm^{-1} 3298 (N-H), 2917 (C-H), 2849 (C-H), 1640 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 2H, N*H*), 5.43 – 5.25 (m, 4H, *H*C=C*H*), 3.41 – 3.32 (m, 4H, HNCH_2), 2.17 (t, *J* = 7.5 Hz, 4H, O=CCH_2CH_2), 2.01 (dt, *J* = 6.6, 6.1 Hz, 8H, =CHCH_2CH_2), 1.66 – 1.52 (m, 4H, O=CCH_2CH_2), 1.39 – 1.19 (m, 42H, CH_2), 0.88 (t, *J* = 6.8 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.69 O=*C*CH_2CH_2), 130.36 (H*C*=*C*H), 130.14 (H*C*=*C*H), 129.84 (H*C*=*C*H), 128.19 (H*C*=*C*H), 128.03 (H*C*=*C*H), 40.29 (HN*C*H_2), 36.82 (O=C*C*H_2CH_2), 32.04 (*C*H_2), 29.90 (*C*H_2), 29.86 (*C*H_2), 29.66 (*C*H_2), 29.45 (*C*H_2), 29.42 (*C*H_2), 29.30 (*C*H_2), 27.35 (CH_2*C*H_2CH=), 27.31 (*C*H_2), 25.86 (O=CCH_2*C*H_2), 22.81 (*C*H_2), 14.25 (*C*H_3).; *m/z* (ES^+) 611.3 $[M+Na]^+$ (2 x C18:1).

(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(ethane-1,2-diyl)dilinoleamide (3.23)



The general procedure for the synthesis of difatty amides was applied using linoleic acid (20 g, 70 mmol, 1.0 equiv.), and ethylene diamine (2.38 mL, 35 mmol, 0.5 equiv.) to give the product as a white solid. (33 %). ν_{max}/cm^{-1} 3302 (N-H), 2924 (C-H), 2853 (C-H), 1638 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (s, 2H, N*H*), 5.43 – 5.26 (m, 6H, *H*C=C*H*), 3.41 – 3.32 (m, 4H, HNC*H*$_2$), 2.77 (t, *J* = 6.4 Hz, 2H, =CHC*H*$_2$CH=), 2.17 (t, *J* = 7.8 Hz, 4H, O=CCH$_2$CH$_2$), 2.08 – 1.91 (m, 8H, =CHC*H*$_2$CH$_2$), 1.67 – 1.54 (m, 4H, O=CCH$_2$C*H*$_2$), 1.41 – 1.19 (m, 36H, CH$_2$), 0.88 (td, *J* = 6.9, 3.8 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.67 (O=CCH$_2$CH$_2$), 130.35 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.83 (H*C*=*C*H), 128.18 (H*C*=*C*H), 128.02 (H*C*=*C*H), 40.28 (HNCH$_2$), 36.81 (O=C*C*H$_2$CH$_2$), 32.03 (*C*H$_2$), 31.65 (*C*H$_2$), 29.89 (*C*H$_2$), 29.86 (*C*H$_2$), 29.83 (*C*H$_2$), 29.76 (*C*H$_2$), 29.66 (*C*H$_2$), 29.47 (*C*H$_2$), 29.42 (*C*H$_2$), 29.30 (*C*H$_2$), 27.32 (CH$_2$*C*H$_2$CH=), 25.85 (O=CCH$_2$*C*H$_2$), 25.75 (*C*H$_2$), 22.81 (*C*H$_2$), 22.70 (*C*H$_2$), 14.24 (*C*H$_3$), 14.20 (*C*H$_3$).; *m/z* (ES$^+$) 611.4 [M+Na]$^+$ (2 x C18:1), 609.4 [M+Na]$^+$ (C18:1, C18:2), 607.4 [M+Na]$^+$ (2 x C18:2).

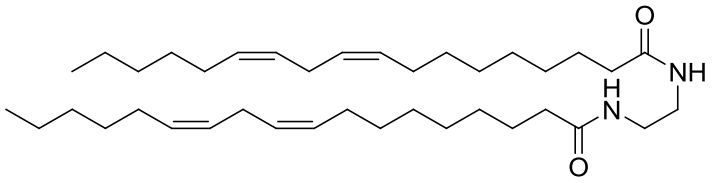
(*Z*)-N,N'-(ethane-1,2-diyl)dioleamide (3.35) (synthesised from rapeseed oil)



The general procedure for the synthesis of difatty amides was applied using rapeseed oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (2.26 mL, 33 mmol, 1.5 equiv.) to give the product as a white solid. (74 %). ν_{max}/cm^{-1} 3314 (N-H), 2926 (C-

H), 2854 (C-H), 1644 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 2H, N*H*), 5.45 – 5.25 (m, 5H, *H*C=C*H*), 3.43 – 3.29 (m, 4H, HNCH_2), 2.82 – 2.73 (m, 1H, =CHCH_2CH=), 2.17 (t, *J* = 7.9 Hz, 4H, O=CCH_2CH_2), 2.11 – 1.94 (m, 8H, =CHCH_2CH_2), 1.67 – 1.54 (m, 4H, O=CCH_2CH_2), 1.40 – 1.20 (m, 40H, CH_2), 0.92 (tt, *J* = 7.5, 7.0, 6.4 Hz, 3H, =CHCH_2CH_3, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.68 (O=*C*CH_2CH_2), 132.06 (H*C*=*C*H), 130.33 (H*C*=*C*H), 130.11 (H*C*=*C*H), 130.04 (H*C*=*C*H), 129.92 (H*C*=*C*H), 129.80 (H*C*=*C*H), 128.40 (H*C*=*C*H), 128.34 (H*C*=*C*H), 128.17 (H*C*=*C*H), 128.00 (H*C*=*C*H), 127.85 (H*C*=*C*H), 127.22 (H*C*=*C*H), 40.21 (HN*C*H_2), 36.78 (O=C*C*H_2CH_2), 32.01 (*C*H_2), 31.89 (*C*H_2), 31.63 (*C*H_2), 29.87 (*C*H_2), 29.85 (*C*H_2), 29.77 (*C*H_2), 29.64 (*C*H_2), 29.43 (*C*H_2), 29.42 (*C*H_2), 29.29 (*C*H_2), 27.33 (CH_2*C*H_2CH=), 27.30 (*C*H_2), 25.86 (O=CCH_2*C*H_2), 22.79 (*C*H_2), 14.39 (=CHCH_2*C*H_3), 14.22 (*C*H_3), 14.18 (*C*H_3).; *m/z* (ES^+) 611.4 $[M+Na]^+$ (2 x C18:1), 609.4 $[M+Na]^+$ (C18:1, C18:2), 607.4 $[M+Na]^+$ (2 x C18:2), 587.4 $[M+Na]^+$ (C18:0, C16:0) 585.4 $[M+Na]^+$ (C18:1, C16:0).

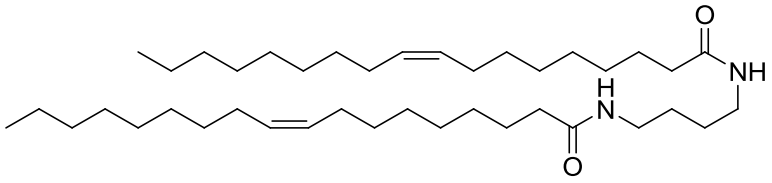
(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(ethane-1,2-diyl)dilinoleamide (3.36) (synthesised from soybean oil)



The general procedure for the synthesis of difatty amides was applied using soybean oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (2.28 mL, 34 mmol, 1.5 equiv.) to give the product as a white solid. (62 %). ν_{max}/cm^{-1} 3303 (N-H), 2923 (C-H), 2852 (C-H), 1637 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (s, 2H, N*H*), 5.45 – 5.26 (m, 5H, *H*C=C*H*), 3.42 – 3.30 (m, 4H, HNCH_2), 2.78 (dd, *J* = 13.7, 7.1 Hz,

2H, =CHC*H*$_2$CH=), 2.17 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.09 – 1.96 (m, 7H, =CHC*H*$_2$CH$_2$), 1.69 – 1.53 (m, 4H, O=CCH$_2$C*H*$_2$), 1.41 – 1.20 (m, 37H, CH$_2$), 0.92 (tt, *J* = 7.5, 7.0, 3.9 Hz, 3H, =CHCH2C*H*$_3$, C*H*$_3$).; ^{13}C NMR (101 MHz, CDCl$_3$) δ 174.65 (O=*C*CH$_2$CH$_2$), 132.09 (H*C*=*C*H), 130.35 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.83 (H*C*=*C*H), 128.36 (H*C*=*C*H), 128.18 (H*C*=*C*H), 128.02 (H*C*=*C*H), 127.86 (H*C*=*C*H), 127.23 (H*C*=*C*H), 40.28 (HN*C*H$_2$), 36.81 (O=C*C*H$_2$CH$_2$), 32.03 (*C*H$_2$), 31.64 (*C*H$_2$), 29.89 (*C*H$_2$), 29.83 (*C*H$_2$), 29.76 (*C*H$_2$), 29.65 (*C*H$_2$), 29.45 (*C*H$_2$), 29.41 (*C*H$_2$), 29.29 (*C*H$_2$), 27.32 (CH$_2$*C*H$_2$CH=), 25.85 (O=CCH$_2$*C*H$_2$), 25.75 (*C*H$_2$), 22.80 (*C*H$_2$), 22.69 (*C*H$_2$), 14.40 (=CHCH$_2$*C*H$_3$), 14.24 (*C*H$_3$), 14.20 (*C*H$_3$).; *m/z* (ES$^+$) 611.4 [M+Na]$^+$ (2 x C18:1), 609.4 [M+Na]$^+$ (C18:1, C18:2), 607.4 [M+Na]$^+$ (2 x C18:2), 585.4 [M+Na]$^+$ (C18:1, C16:0), 583.4 [M+Na]$^+$ (C18:2, C16:0).

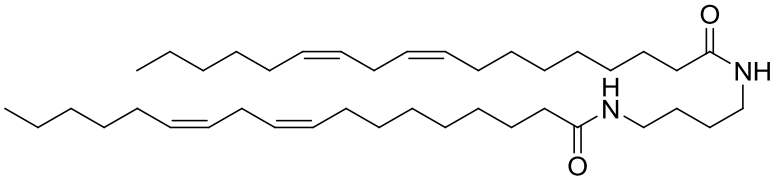
(*Z*)-N,N'-(butane-1,4-diyl)dioleamide (3.47)



The general procedure for the synthesis of difatty amides was applied using oleic acid (20 g, 71 mmol, 1.0 equiv.), and ethylene diamine (3.56 mL, 36 mmol, 0.5 equiv.) to give the product as a white solid. (31 %) ν_{max}/cm^{-1} 3299 (N-H), 2918 (C-H), 2850 (C-H), 1631 (C=O).; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.77 (t, *J* = 6.3 Hz, 2H, N*H*), 5.44 – 5.24 (m, 4H, *H*C=C*H*), 3.27 (dt, *J* = 5.7 Hz, 4H, HNC*H*$_2$CH$_2$), 2.16 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.05 – 1.94 (m, 8H, =CHC*H*$_2$), 1.69 – 1.57 (m, 4H, O=CCH$_2$C*H*$_2$), 1.53 (t, *J* = 6.3 Hz, 4H, HNCH$_2$C*H*$_2$), 1.42 – 1.18 (m, 41H, C*H*$_2$), 0.88 (t, *J* = 6.6 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.56 (O=*C*CH$_2$CH$_2$), 130.14 (H*C*=*C*H), 129.88 (H*C*=*C*H), 39.10 (HN*C*H$_2$CH$_2$), 36.99

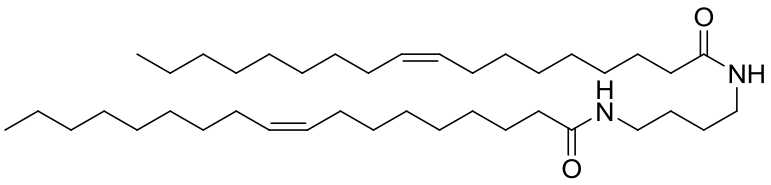
(O=C*C*H$_2$CH$_2$), 32.05 (*C*H$_2$), 29.91 (*C*H$_2$), 29.86 (*C*H$_2$), 29.67 (*C*H$_2$), 29.46 (*C*H$_2$), 29.42 (*C*H$_2$), 29.30 (*C*H$_2$), 27.36 (*C*H$_2$), 27.32 (*C*H$_2$), 27.09 (HNCH$_2$*C*H$_2$), 25.94 (=CH*C*H$_2$), 22.82 (*C*H$_2$), 14.26 (*C*H$_3$).; *m/z* (ES$^+$) 639.3 [M+Na]$^+$ (C18:1).

(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(butane-1,4-diyl)dilinoleamide (3.48)



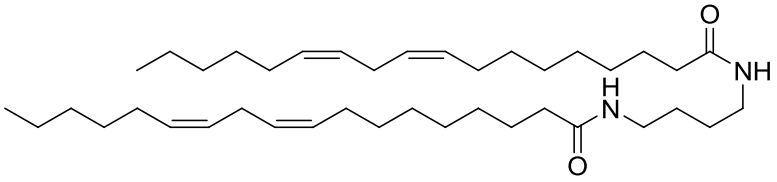
The general procedure for the synthesis of difatty amides was applied using linoleic acid (20 g, 71 mmol, 1.0 equiv.), and ethylene diamine (3.58 mL, 36 mmol, 0.5 equiv.) to give the product as a white solid. (34 %) ν_{max}/cm^{-1} 3298 (N-H), 2917 (C-H), 2849 (C-H) 1631 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (t, *J* = 6.0 Hz, 2H, N*H*), 5.43 – 5.27 (m, 6H, *H*C=C*H*), 3.27 (dt, *J* = 6.3 Hz, 4H, HNC*H*$_2$CH$_2$), 2.77 (t, *J* = 6.5 Hz, 2H, =CHC*H*$_2$CH=), 2.16 (t, *J* = 7.8 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.03 (m, 8H, =CHC*H*$_2$), 1.68 – 1.56 (m, 4H, O=CCH$_2$CH$_2$), 1.56 – 1.49 (m, 4H, HNCH$_2$C*H*$_2$), 1.41 – 1.20 (m, 36H, C*H*$_2$), 0.89 (dt, *J* = 6.9, 3.8 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54 (O=*C*CH$_2$CH$_2$), 130.36 (H*C*=*C*H), 130.17 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.86 (H*C*=*C*H), 128.17 (H*C*=*C*H), 128.03 (H*C*=*C*H), 39.10 (HN*C*H$_2$CH$_2$), 36.96 (O=C*C*H$_2$CH$_2$), 32.03 (*C*H$_2$), 31.65 (*C*H$_2$), 29.89 (*C*H$_2$), 29.85 (*C*H$_2$), 29.75 (*C*H$_2$), 29.65 (*C*H$_2$), 29.47 (*C*H$_2$), 29.45 (*C*H$_2$), 29.42 (*C*H$_2$), 29.29 (*C*H$_2$), 27.32 (=CH*C*H$_2$CH=), 27.08 (HNCH$_2$*C*H$_2$), 25.93 (*C*H$_2$), 25.75 (=CH*C*H$_2$), 22.81 (*C*H$_2$), 22.70 (*C*H$_2$), 14.25 (*C*H$_3$), 14.20 (*C*H$_3$).;*m/z* (ES$^+$) 639.3 [M+Na]$^+$ (2 x C18:1) 637.3 [M+Na]$^+$ (C18:1, C18:2), 635.3 [M+Na]$^+$ (2 x C18:2).

(*Z*)-N,N'-(butane-1,4-diyl)dioleamide (3.49) (synthesised from rapeseed oil)



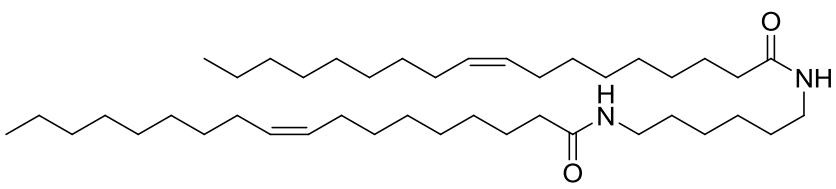
The general procedure for the synthesis of difatty amides was applied using rapeseed oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (3.41 mL, 34 mmol, 1.5 equiv.) to give the product as a white solid. (81 %) ν_{max}/cm^{-1} 3302 (N-H), 2918 (C-H), 2849 (C-H) 1631 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (t, *J* = 5.7 Hz, 2H, N*H*), 5.44 – 5.26 (m, 5H, *H*C=C*H*), 3.27 (dt, *J* = 6.3, 5.7 Hz, 4H, HNC*H*$_2$CH$_2$), 2.86 – 2.70 (m, 1H, =CHC*H*$_2$CH=), 2.16 (t, *J* = 7.8 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.10 – 1.94 (m, 8H, =CHC*H*$_2$), 1.69 – 1.57 (m, 4H, O=CCH$_2$C*H*$_2$), 1.57 – 1.49 (m, 4H, HNCH$_2$C*H*$_2$), 1.42 – 1.17 (m, 39H, C*H*$_2$), 0.92 (tt, *J* = 7.5, 7.0, 3.8 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58 (O=*C*CH$_2$CH$_2$), 132.10 (H*C*=*C*H), 130.36 (H*C*=*C*H), 130.17 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.86 (H*C*=*C*H), 128.42 (H*C*=*C*H), 128.18 (H*C*=*C*H), 128.03 (H*C*=*C*H), 127.86 (H*C*=*C*H), 127.24 (H*C*=*C*H), 39.10 (HN*C*H$_2$CH$_2$), 36.96 (O=C*C*H$_2$CH$_2$), 32.03 (*C*H$_2$), 31.65 (*C*H$_2$), 29.90 (*C*H$_2$), 29.86 (*C*H$_2$), 29.66 (*C*H$_2$), 29.45 (*C*H$_2$), 29.42 (*C*H$_2$), 29.29 (*C*H$_2$), 27.43 (*C*H$_2$), 27.35 (*C*H$_2$), 27.31 (=CH*C*H$_2$CH=), 27.07 (HNCH$_2$*C*H$_2$), 25.93 (*C*H$_2$), 25.75 (=CH*C*H$_2$), 22.81 (*C*H$_2$), 22.70 (*C*H$_2$), 20.68 (*C*H$_2$), 14.25 (*C*H$_3$), 14.21 (*C*H$_3$).; *m/z* (ES$^+$) 639.3 [M+Na]$^+$ (2 x C18:1) 637.3 [M+Na]$^+$ (C18:1, C18:2), 635.3 [M+Na]$^+$ (2 x C18:2) 615.2 [M+Na]$^+$ (C18:0, C16:0) 613.2 [M+Na]$^+$ (C18:1, C16:0).

(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(butane-1,4-diyl)dilinoleamide (3.50) (synthesised from soybean oil)



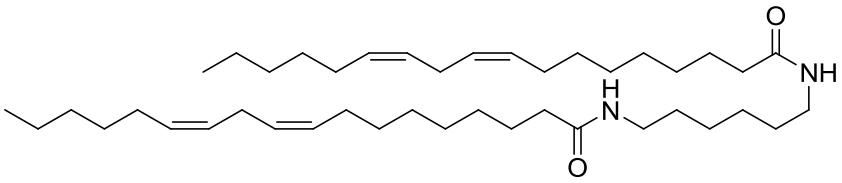
The general procedure for the synthesis of difatty amides was applied using soybean oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (3.44 g, 34 mmol, 1.5 equiv.) to give the product as a white solid. (78 %) ν_{max}/cm^{-1} 3303 (N-H), 2923 (C-H), 2852 (C-H) 1632 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, *J* = 5.7 Hz, 2H, N*H*), 5.45 – 5.26 (m, 6H, *H*C=C*H*), 3.27 (dt, *J* = 6.1, 5.8 Hz, 4H, HNC*H*$_2$CH$_2$), 2.77 (t, *J* = 6.5 Hz, 2H, =CHC*H*$_2$CH=), 2.16 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.11 – 1.91 (m, 8H, =CHC*H*$_2$), 1.68 – 1.56 (m, 4H, O=CCH$_2$C*H*$_2$), 1.53 (t, *J* = 6.4 Hz, 4H, HNCH$_2$C*H*$_2$), 1.41 – 1.19 (m, 36H, C*H*$_2$), 1.01 – 0.83 (m, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.55 (O=*C*CH$_2$CH$_2$), 130.36 (H*C*=*C*H), 130.17 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.87 (H*C*=*C*H), 128.38 (H*C*=*C*H), 128.18 (H*C*=*C*H), 128.04 (H*C*=*C*H), 127.86 (H*C*=*C*H), 39.10 (HN*C*H$_2$CH$_2$), 36.97 (O=C*C*H$_2$CH$_2$), 32.04 (*C*H$_2$), 31.65 (*C*H$_2$), 29.90 (*C*H$_2$), 29.83 (*C*H$_2$), 29.76 (*C*H$_2$), 29.66 (*C*H$_2$), 29.48 (*C*H$_2$), 29.45 (*C*H$_2$), 29.42 (*C*H$_2$), 29.29 (*C*H$_2$), 27.33 (=CH*C*H$_2$CH=), 27.08 (HNCH$_2$*C*H$_2$), 25.93 (*C*H$_2$), 25.76 (=CH*C*H$_2$), 22.81 (*C*H$_2$), 22.70 (*C*H$_2$), 14.25 (*C*H$_3$), 14.21 (*C*H$_3$).; *m/z* (ES$^+$) 639.3 [M+Na]$^+$ (2 x C18:1) 637.3 [M+Na]$^+$ (C18:1, C18:2), 635.3 [M+Na]$^+$ (2 x C18:2) 615.2 [M+Na]$^+$ (C18:0, C16:0) 613.2 [M+Na]$^+$ (C18:1, C16:0), 613.2 [M+Na]$^+$ (C18:2, C16:0).

(*Z*)-N,N'-(hexane-1,6-diyl)dioleamide (3.51)



The general procedure for the synthesis of difatty amides was applied using oleic acid (20 g, 71 mmol, 1.0 equiv.), and ethylene diamine (4.62 mL, 36 mmol, 0.5 equiv.) to give the product as a white solid. (40 %). ν_{max}/cm^{-1} 3302 (N-H), 2917 (C-H), 2849 (C-H) 1632 (C=O);; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (t, *J* = 4.6 Hz, 2H, N*H*), 5.43 – 5.25 (m, 4H, *H*C=C*H*), 3.24 (dt, *J* = 6.6 Hz, 4H, HNC$H_2$$CH_2$$CH_2$), 2.16 (t, *J* = 7.6 Hz, 4H, O=CC$H_2$$CH_2$), 2.01 (dt, *J* = 6.3 Hz, 8H, =CHCH_2), 1.70 – 1.55 (m, 4H, O=CCH_2CH_2), 1.55 – 1.43 (m, 4H, HNCH_2C$H_2$$CH_2$), 1.41 – 1.19 (m, 46H, HN$CH_2$$CH_2CH_2$, C$H_2$), 0.88 (t, *J* = 6.6 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.36 (O=*C*$CH_2$$CH_2$), 130.35 (H*C*=*C*H), 130.12 (H*C*=*C*H), 129.87 (H*C*=*C*H), 128.16 (H*C*=*C*H), 128.03 (H*C*=*C*H), 39.02 (HN*C*$H_2$$CH_2$$CH_2$), 37.01 (O=C*C*$H_2$$CH_2$), 32.03 (*C*$H_2$), 29.89 (*C*$H_2$), 29.85 (*C*$H_2$), 29.65 (*C*$H_2$), 29.62 (HN$CH_2$*C*$H_2$$CH_2$), 29.45 (*C*$H_2$), 29.30 (*C*$H_2$), 27.44 (*C*$H_2$), 27.35 (=CH*C*$H_2$), 27.31 (*C*$H_2$), 26.07 (*C*$H_2$), 25.96 (O=C$CH_2$*C*$H_2$), 22.81 (*C*$H_2$), 14.24 (*C*$H_3$).; *m/z* ($ES^+$) 667.3 $[M+Na]^+$ (2 x C18:1) 665.3 $[M+Na]^+$ (C18:1, C18:2),

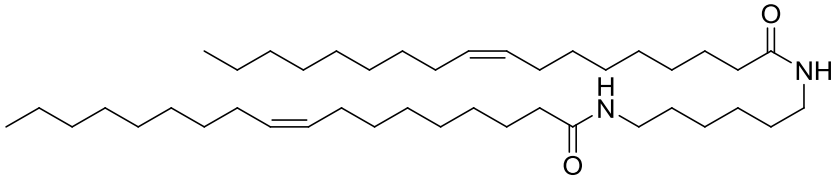
(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(hexane-1,6-diyl)dilinoleamide (3.52)



The general procedure for the synthesis of difatty amides was applied using linoleic acid (20 g, 71 mmol, 1.0 equiv.), and ethylene diamine (4.66 mL, 36 mmol, 0.5 equiv.) to give the product as a white solid. (38 %). ν_{max}/cm^{-1} 3303 (N-H), 2918 (C-H), 2850 (C-H) 1631 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (t, *J* = 6.2 Hz, 2H, N*H*), 5.43 – 5.27 (m, 6H, *H*C=C*H*), 3.24 (q, *J* = 6.6 Hz, 4H, HNC$H_2$$CH_2$$CH_2$), 2.77 (t, *J* = 6.4 Hz, 2H, =CHCH_2CH=), 2.16 (t, *J* = 7.6 Hz, 4H, O=CC$H_2$$CH_2$), 2.10 – 1.92 (m, 8H, =CHCH_2), 1.67 – 1.55 (m, 4H, O=CHCH_2CH_2), 1.55 – 1.40 (m, 4H,

HNCH$_2$C*H*$_2$CH$_2$), 1.40 – 1.09 (m, 39H, HNCH$_2$CH$_2$C*H*$_2$, C*H*$_2$), 0.88 (dt, *J* = 6.9, 6.4, 3.8 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.38 (O=*C*CH$_2$CH$_2$), 130.35 (H*C*=*C*H), 130.17 (H*C*=*C*H), 130.12 (H*C*=*C*H), 129.87 (H*C*=*C*H), 128.16 (H*C*=*C*H), 128.03 (H*C*=*C*H), 39.03 (HN*C*H$_2$CH$_2$CH$_2$), 37.00 (O=C*C*H$_2$CH$_2$), 32.03 (*C*H$_2$), 31.65 (*C*H$_2$), 29.89 (*C*H$_2$), 29.85 (*C*H$_2$), 29.75 (*C*H$_2$), 29.62 (HNCH$_2$*C*H$_2$CH$_2$), 29.47 (*C*H$_2$), 29.44 (*C*H$_2$), 29.29 (*C*H$_2$), 27.32 (=CH*C*H$_2$), 26.07 (*C*H$_2$), 25.96 (O=CCH$_2$*C*H$_2$), 25.75 (*C*H$_2$), 22.81 (*C*H$_2$), 22.70 (*C*H$_2$), 14.24 (*C*H$_3$), 14.20 (*C*H$_3$).; *m/z* (ES$^+$) 667.3 [M+Na]$^+$ (2 x C18:1), 665.3 [M+Na]$^+$ (C18:1, C18:2), 663.3 [M+Na]$^+$ (2 x C18:2).

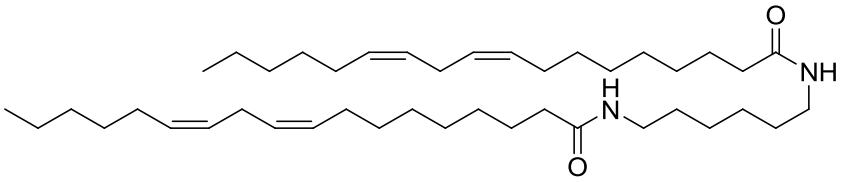
(*Z*)-N,N'-(hexane-1,6-diyl)dioleamide (3.53) (synthesised from rapeseed oil)



The general procedure for the synthesis of difatty amides was applied using rapeseed oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (4.43 mL, 33 mmol, 1.5 equiv.) to give the product as a white solid. (35 %) ν_{max}/cm^{-1} 3308 (N-H), 2919 (C-H), 2851 (C-H) 1633 (C=O); ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.62 (t, *J* = 5.4 Hz, 2H N*H*), 5.43 – 5.25 (m, 5H, *H*C=C*H*), 3.24 (dt, *J* = 6.6, 5.4 Hz, 4H, HNC*H*$_2$CH$_2$CH$_2$), 2.84 – 2.73 (m, 1H, =CHC*H*$_2$CH=), 2.16 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 2.11 – 1.91 (m, 8H, =CHC*H*$_2$), 1.68 – 1.55 (m, 4H, O=CCH$_2$C*H*$_2$), 1.55 – 1.41 (m, 4H, HNCH$_2$C*H*$_2$CH$_2$), 1.41 – 1.20 (m, 43H, HNCH$_2$CH$_2$C*H*$_2$, C*H*$_2$), 0.93 (dt, *J* = 13.0, 7.3 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.36 (O=*C*CH$_2$CH$_2$), 132.10 (H*C*=*C*H), 130.36 (H*C*=*C*H), 130.18 (H*C*=*C*H), 130.13 (H*C*=*C*H), 129.88 (H*C*=*C*H), 128.42 (H*C*=*C*H), 128.17 (H*C*=*C*H), 128.04 (H*C*=*C*H), 127.85

(H*C*=*C*H), 39.03 (HN*C*H_2CH_2CH_2), 37.02 (O=C*C*H_2CH_2), 32.04 (*C*H_2), 31.66 (*C*H_2), 29.90 (*C*H_2), 29.85 (*C*H_2), 29.66 (*C*H_2), 29.63 (HNCH_2*C*H_2CH_2), 29.45 (*C*H_2), 29.30 (*C*H_2), 27.35 (*C*H_2), 27.32 (=CH*C*H_2), 26.07 (*C*H_2), 25.96 (O=CCH_2*C*H_2), 25.76 (*C*H_2), 22.81 (*C*H_2), 22.70 (*C*H_2), 14.25 (*C*H_3).; *m/z* (ES^+) 667.3 $[M+Na]^+$ (2 x C18:1), 665.3 $[M+Na]^+$ (C18:1, C18:2), 663.3 $[M+Na]^+$ (2 x C18:2), 643.3 $[M+Na]^+$ (C18:0, C16:0) 641.3 $[M+Na]^+$ (C18:1, C16:0).

(9*Z*,9'*Z*,12*Z*,12'*Z*)-N,N'-(hexane-1,6-diyl)dilinoleamide (3.54) (synthesised from soybean oil)



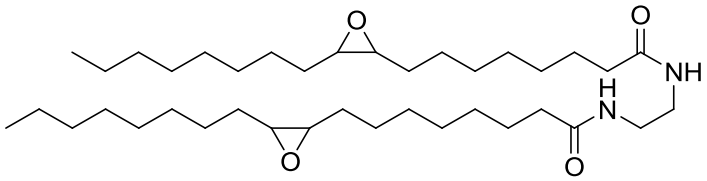
The general procedure for the synthesis of difatty amides was applied using soybean oil (20 g, 23 mmol, 1.0 equiv.), and ethylene diamine (4.47 mL, 34 mmol, 1.5 equiv.) to give the product as a white solid. (35 %). ν_{max}/cm^{-1} 3307 (N-H), 2919 (C-H), 2851 (C-H) 1632 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (t, *J* = 5.6 Hz, 2H N*H*), 5.44 – 5.24 (m, 5H, *H*C=C*H*), 3.24 (dt, *J* = 6.6, 5.6 Hz, 4H, HNCH_2CH_2CH_2), 2.77 (t, *J* = 6.4 Hz, 2H, =CHCH_2CH=), 2.16 (t, *J* = 7.6 Hz, 4H, O=CCH_2CH_2), 2.11 – 1.91 (m, 8H, =CHCH_2), 1.70 – 1.55 (m, 4H, O=CCH_2CH_2), 1.55 – 1.42 (m, 4H, HNCH_2CH_2CH_2), 1.42 – 1.20 (m, 41H, HNCH_2CH_2CH_2, CH_2), 0.92 (dt, *J* = 6.9, 4.0 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.34 (O=*C*CH_2CH_2), 132.09 (H*C*=*C*H), 130.34 (H*C*=*C*H), 130.17 (H*C*=*C*H), 130.11 (H*C*=*C*H), 129.86 (H*C*=*C*H), 128.37 (H*C*=*C*H), 128.16 (H*C*=*C*H), 128.02 (H*C*=*C*H), 127.84

(H*C*=*C*H), 127.23 (H*C*=*C*H), 39.02 (HN*C*H_2CH$_2$CH$_2$), 36.99 (O=C*C*H_2CH$_2$), 32.02 (*C*H_2), 31.64 (*C*H_2), 29.88 (*C*H_2), 29.82 (*C*H_2), 29.75 (*C*H_2), 29.62 (HNCH$_2$*C*H_2CH$_2$), 29.47 (*C*H_2), 29.44 (*C*H_2), 29.29 (*C*H_2), 27.32 (=CH*C*H_2), 26.07 (*C*H_2), 25.95 (O=CCH$_2$*C*H_2), 25.75 (*C*H_2), 22.80 (*C*H_2), 22.69 (*C*H_2), 14.24 (*C*H_3), 14.20 (*C*H_3).;n *m/z* (ES$^+$) 667.3 $[M+Na]^+$ (2 x C18:1), 665.3 $[M+Na]^+$ (C18:1, C18:2), 663.3 $[M+Na]^+$ (2 x C18:2), 643.3 $[M+Na]^+$ (C18:0, C16:0) 641.3 $[M+Na]^+$ (C18:1, C16:0), 639.3 $[M+Na]^+$ (C18:2, C16:0).

6.3.2 General Procedure for the epoxidation of difatty amides

The desired difatty amide (1 equiv.) was dissolved in DCM (0.15 M) at RT. Peracetic acid (2.5 equiv for oleic and 5 equiv for linoleic, rapeseed oil and soybean oil) was added and left to react for 2 hours. The reaction mixture was washed with 15 % NaCl, separated and dried over $MgSO_4$. The solvent was removed in *vacuo.* to give pure product.

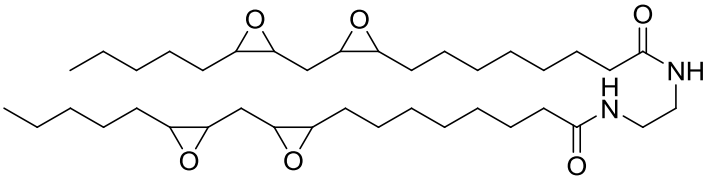
N,N'-(ethane-1,2-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.21)



The general procedure for the epoxidation of difatty amides was applied using **3.20** (14.17 g, 24 mmol, 1.0 equiv.), and peracetic acid (10.2 mL, 60 mmol, 2.5 equiv.) to give product as a white solid (85 %); ν_{max}/cm^{-1} 3310 (N-H), 2917 (C-H), 2849 (C-H), 1638 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 2H, N*H*), 3.43 – 3.30 (m, 4H, HNC*H*$_2$), 3.13 – 2.80 (m, 4H, *H*C(O)C*H*), 2.17 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 1.67 – 1.57 (m, 4H, O=CCH$_2$C*H*$_2$), 1.51 – 1.39 (m, 14H, C*H*$_2$CH(O), C*H*$_2$), 1.39 –

1.20 (m, 34H, CH_2), 0.88 (t, J = 6.5 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.62 (O=CCH_2CH_2), 57.38 (HC(O)CH), 57.34 (HC(O)CH), 40.36 (HNCH$_2$), 36.76 (O=CCH$_2$CH$_2$), 31.99 (CH$_2$), 29.68 (CH$_2$), 29.47 (CH$_2$), 29.35 (CH$_2$), 29.27 (CH$_2$), 27.98 (CH$_2$CH(O)), 27.92 (CH$_2$), 26.74 (CH$_2$), 25.78 (O=CCH$_2$$CH_2$), 22.79 ($CH_2$), 14.24 ($CH_3$).; *m/z* (ES$^+$) 643.4 [M+Na]$^+$ 657.4 [M+Na]$^+$ (C18:1, C18:2), (2 x C18:1).

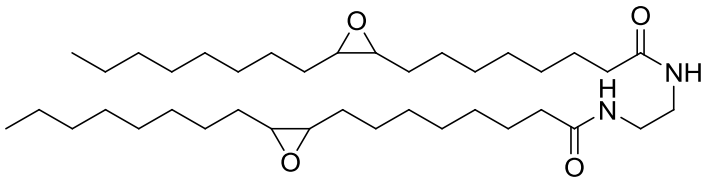
N,N'-(ethane-1,2-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.24)



The general procedure for the epoxidation of difatty amides was applied using **3.23** (13.93 g, 24 mmol, 1.0 equiv.), and peracetic acid (20.2 mL, 119 mmol, 5.0 equiv.) to give product as a white solid (81 %); ν_{max}/cm^{-1} 3303 (N-H), 2920 (C-H), 2851 (C-H), 1638 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (s, 2H, NH), 3.42 – 3.29 (m, 4H, HNCH_2), 3.26 – 2.78 (m, 5H, HC(O)CH), 2.17 (t, J = 7.6 Hz, 4H, O=CCH_2CH$_2$), 1.82 – 1.69 (m, 2H, (O)CHCH_2CH(O)), 1.69 – 1.56 (m, 4H, O=CCH$_2$CH_2), 1.56 – 1.40 (m, 14H, (O)CHCH_2, CH_2), 1.40 – 1.15 (m, 28H, CH_2), 0.89 (dt, J = 7.0 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.77 (O=CCH$_2$CH$_2$), 57.38 (HC(O)CH), 57.35 (HC(O)CH), 57.17 (HC(O)CH), 57.11 (HC(O)CH), 56.88 (HC(O)CH), 56.81 (HC(O)CH), 54.48 (HC(O)CH), 54.35 (HC(O)CH), 40.22 (HNCH$_2$), 36.69 (O=CCH$_2$CH$_2$), 31.95 (CH$_2$), 31.76 (CH$_2$),

29.80 (*C*H_2), 29.65 (*C*H_2), 29.44 (*C*H_2), 29.39 (*C*H_2), 29.32 (*C*H_2), 29.23 (*C*H_2), 27.98 (*C*H_2CH(O)), 27.94 (*C*H_2), 27.89 (*C*H_2), 27.30 (*C*H_2), 27.02 ((O)CH*C*H_2CH(O)), 26.71 (*C*H_2), 26.67 (*C*H_2), 26.56 (*C*H_2), 26.35 (*C*H_2), 26.24 (*C*H_2), 25.84 (O=CCH$_2$*C*H_2), 25.73 (*C*H_2), 22.76 (*C*H_2), 22.66 (*C*H_2), 14.21 (*C*H_3), 14.09 (*C*H_3).; *m/z* (ES^+) 671.4 $[M+Na]^+$ (2 x C18:2), 657.4 $[M+Na]^+$ (C18:1, C18:2), 643.4 $[M+Na]^+$ (2 x C18:1).

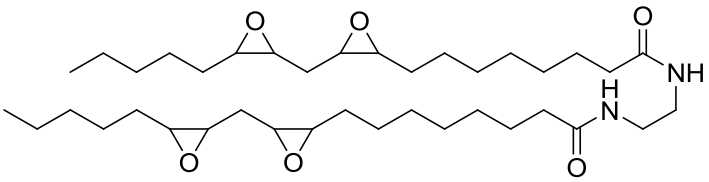
N,N'-(ethane-1,2-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.37) (synthesised from rapeseed oil)



The general procedure for the epoxidation of difatty amides was applied using **3.35** (9.7 g, 17 mmol, 1.0 equiv.), and peracetic acid (14.0 mL, 83 mmol, 5.0 equiv.) to give product as a white solid (98 %); ν_{max}/cm^{-1} 3304 (N-H), 2918 (C-H), 2850 (C-H), 1637 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (s, 2H, N*H*), 3.44 – 3.27 (m, 4H, HNC*H*$_2$), 3.24 – 2.83 (m, 4H, *H*C(O)C*H*), 2.17 (t, *J* = 7.8 Hz, 4H, O=CC*H*$_2$CH$_2$), 1.84 – 1.69 (m, 1H, (O)CHC*H*$_2$CH(O)), 1.65 – 1.57 (m, 4H, O=CCH$_2$C*H*$_2$), 1.56 – 1.40 (m, 14H, (O)CHC*H*$_2$, C*H*$_2$), 1.37 – 1.23 (m, 34H, C*H*$_2$), 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.67 (O=C*C*H$_2$CH$_2$), 57.37 (H*C*(O)*C*H), 57.34 (H*C*(O)*C*H), 57.17 (H*C*(O)*C*H), 57.11 (H*C*(O)*C*H), 56.88 (H*C*(O)*C*H), 54.47 (H*C*(O)*C*H), 54.33 (H*C*(O)*C*H), 54.18 (H*C*(O)*C*H), 40.29 (HN*C*H$_2$), 36.73 (O=C*C*H$_2$CH$_2$), 31.97 (*C*H_2), 31.78 (*C*H_2), 29.82 (*C*H_2), 29.65 (*C*H_2), 29.46 (*C*H_2), 29.34 (*C*H_2), 29.26 (*C*H_2), 27.96 (*C*H_2CH(O)), 27.90 (*C*H_2), 27.32 (*C*H_2), 26.73

(CH_2), 26.26 (CH_2), 25.86 (O=CCH_2CH_2), 25.76 (CH_2), 22.77 (CH_2), 22.68 (CH_2), 14.22 (CH_3), 14.10 (CH_3).; *m/z* (ES^+) 671.4 $[M+Na]^+$ (2 x C18:2), 657.4 $[M+Na]^+$ (C18:1, C18:2), 643.4 $[M+Na]^+$ (2 x C18:1), 615.4 $[M+Na]^+$ (C18:2, C16:0), 601.4 $[M+Na]^+$ (C18:1, C16:0).

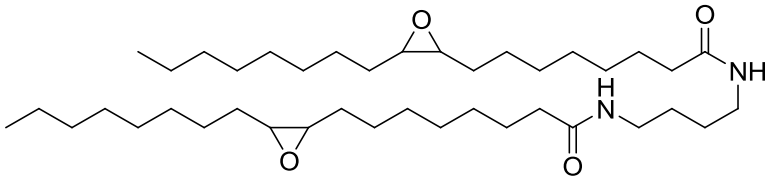
N,N'-(ethane-1,2-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.38)



The general procedure for the epoxidation of difatty amides was applied using **3.36** (8.14 g, 14 mmol, 1.0 equiv.), and peracetic acid (11.75 mL, 70 mmol, 5.0 equiv.) to give product as a white solid (96 %); ν_{max}/cm^{-1} 3305 (N-H), 2917 (C-H), 2849 (C-H), 1637 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 2H, N*H*), 3.42 – 3.32 (m, 4H, HNCH_2), 3.16 – 2.84 (m, 5H, *H*C(O)C*H*), 2.17 (t, *J* = 7.6 Hz, 4H, O=CCH_2CH_2), 1.81 – 1.69 (m, 2H, (O)CHCH_2CH(O)), 1.64 – 1.58 (m, 4H, O=CCH_2CH_2), 1.52 (dd, *J* = 16.3, 6.7 Hz, 12H, (O)CHCH_2, CH_2), 1.37 – 1.22 (m, 32H, CH_2), 0.89 (dt, *J* = 9.4, 7.2 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.63 (O=*C*CH_2CH_2), 57.38 (H*C*(O)*C*H), 57.34 (H*C*(O)*C*H), 57.17 (H*C*(O)*C*H), 57.11 (H*C*(O)*C*H), 56.88 (H*C*(O)*C*H), 56.82 (H*C*(O)*C*H), 54.49 (H*C*(O)*C*H), 54.35 (H*C*(O)*C*H), 40.31 (HN*C*H_2), 36.82 (O=CCH_2CH_2), 32.04 (CH_2), 31.97 (CH_2), 31.78 (CH_2), 29.82 (CH_2), 29.65 (CH_2), 29.48 (CH_2), 29.41 (CH_2), 29.34 (CH_2), 29.25 (CH_2), 28.00 (CH_2), 27.96 (*C*H_2CH(O)), 27.90 (CH_2), 27.32 (CH_2), 27.05 ((O)CH*C*H_2CH(O)),

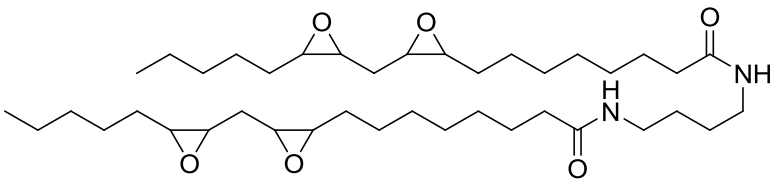
26.73 (CH_2), 26.68 (CH_2), 26.58 (CH_2), 26.36 (CH_2), 26.26 (CH_2), 25.86 (O=CCH_2*C*H_2), 25.75 (CH_2), 22.78 (CH_2), 22.69 (CH_2), 14.22 (CH_3), 14.11 (CH_3).; *m/z* (ES^+) 671.4 $[M+Na]^+$ (2 x C18:2), 657.4 $[M+Na]^+$ (C18:1, C18:2), 643.4 $[M+Na]^+$ (2 x C18:1), 615.4 $[M+Na]^+$ (C18:2, C16:0), 601.4 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(butane-1,4-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.55)



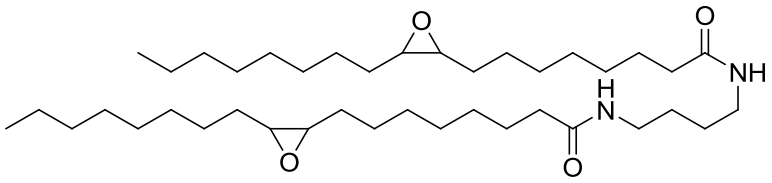
The general procedure for the epoxidation of difatty amides was applied using **3.47** (13.67 g, 22 mmol, 1.0 equiv.), and peracetic acid (9.4 mL, 55 mmol, 2.5 equiv.) to give product as a white solid (88 %); ν_{max}/cm^{-1} 3299 (N-H), 2918 (C-H), 2850 (C-H), 1631 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08 (s, 2H, N*H*), 3.48 – 3.16 (m, 4H, HNC$H_2$$CH_2$), 2.90 (s, 3H, *H*C(O)C*H*), 2.17 (t, *J* = 7.5 Hz, 4H, O=CC$H_2$$CH_2$), 1.87 – 1.15 (m, 57H, O=CCH_2CH_2, (O)CHCH_2, HNCH_2CH_2, CH_2), 0.88 (t, *J* = 6.4 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.56 (O=*C*$CH_2$$CH_2$), 57.34 (H*C*(O)*C*H), 39.07 (HN*C*H_2), 36.79 (O=C*C*$H_2$$CH_2$), 31.92 ($CH_2$), 29.62 ($CH_2$), 29.42 (O=C$CH_2$*C*$H_2$), 29.32 ($CH_2$), 29.29 ($CH_2$), 27.91 ($CH_2$), 27.86 ($CH_2$), 27.02 ($CH_2$), 26.68 ($CH_2$), 25.82 ($CH_2$), 22.74 ($CH_2$), 14.18 ($CH_3$).; *m/z* ($ES^+$) 671.5 $[M+Na]^+$ (2 x C18:1).

N,N'-(butane-1,4-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.56)



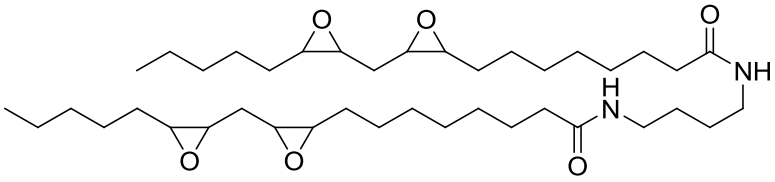
The general procedure for the epoxidation of difatty amides was applied using **3.48** (14.71 g, 23 mmol, 1.0 equiv.), and peracetic acid (19.6 mL, 116 mmol, 5.0 equiv.) to give product as a white solid (81 %); ν_{max}/cm^{-1} 3305 (N-H), 2918 (C-H), 2850 (C-H), 1632 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 2H, N*H*), 3.33 – 3.18 (m, 4H, HN*C*H$_2$CH$_2$), 3.17 – 2.81 (m, 6H, *H*C(O)C*H*), 2.17 (t, *J* = 7.6 Hz, 4H, O=CCH$_2$CH$_2$), 1.81 – 1.69 (m, 2H, (O)CHC*H*$_2$CH(O)), 1.68 – 1.58 (m, 4H, O=CC*H*$_2$CH$_2$), 1.56 – 1.43 (m, 16H, O=CCH$_2$CH$_2$, (O)CHC*H*$_2$, HNCH$_2$C*H*$_2$), 1.42 – 1.18 (m, 28H, C*H*$_2$), 0.89 (dt, *J* = 6.8 Hz, 6H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.50 (O=*C*CH$_2$CH$_2$), 57.29 (H*C*(O)*C*H), 57.08 (H*C*(O)*C*H), 57.04 (H*C*(O)*C*H), 56.78 (H*C*(O)*C*H), 56.74 (H*C*(O)*C*H), 54.39 (H*C*(O)*C*H), 54.26 (H*C*(O)*C*H), 39.03 (HN*C*H$_2$CH$_2$), 36.71 (O=C*C*H$_2$CH$_2$), 31.87 (*C*H$_2$), 31.68 (*C*H$_2$), 29.72 (*C*H$_2$), 29.56 (*C*H$_2$), 29.38 (*C*H$_2$), 29.31 (*C*H$_2$), 29.24 (*C*H$_2$), 27.89 (*C*H$_2$), 27.82 (*C*H$_2$), 27.21 (O=CCH$_2$*C*H$_2$), 26.96 (*C*H$_2$), 26.63 (*C*H$_2$), 26.49 (*C*H$_2$), 26.27 (*C*H$_2$), 26.16 (*C*H$_2$), 25.76 (*C*H$_2$), 22.68 (*C*H$_2$), 22.59 (*C*H$_2$), 14.14 (*C*H$_3$), 14.02 (*C*H$_3$).; *m/z* (ES$^+$) 699.4 [M+Na]$^+$ (2 x C18:2), 685.4 [M+Na]$^+$ (C18:1, C18:2), 671.5 [M+Na]$^+$ (2 x C18:1).

N,N'-(butane-1,4-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.57) (synthesised from rapeseed oil)



The general procedure for the epoxidation of difatty amides was applied using **3.49** (11.77 g, 19 mmol, 1.0 equiv.), and peracetic acid (18.7 mL, 95 mmol, 5.0 equiv.) to give product as a white solid (85 %); ν_{max}/cm^{-1} 3306 (N-H), 2917 (C-H), 2850 (C-H), 1632 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, 2H, N*H*), 3.27 (dt, *J* = 6.2 Hz, 4H, HNC*H*$_2$CH$_2$), 3.21 – 2.80 (m, 4H, *H*C(O)C*H*), 2.17 (t, *J* = 7.6 Hz, 4H, O=CC*H*$_2$CH$_2$), 1.82 – 1.69 (m, 2H, (O)CHC*H*$_2$CH(O)), 1.66 – 1.59 (m, 4H, O=CCH$_2$C*H*$_2$), 1.55 – 1.40 (m, 16H, O=CCH$_2$CH$_2$, (O)CHC*H*$_2$, HNCH$_2$C*H*$_2$), 1.40 – 1.21 (m, 33H, CH$_2$), 0.89 (dt, *J* = 10.8, 7.2 Hz, 6H, CH$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.56 (O=*C*CH$_2$CH$_2$), 57.34 (H*C*(O)*C*H), 39.07 (HN*C*H$_2$CH$_2$), 36.79 (O=C*C*H$_2$CH$_2$), 31.92 (*C*H$_2$), 29.62 (*C*H$_2$), 29.42 (*C*H$_2$), 29.32 (*C*H$_2$), 29.29 (*C*H$_2$), 27.91 (*C*H$_2$), 27.86 (*C*H$_2$), 27.02 (O=CCH$_2$*C*H$_2$), 26.68 (*C*H$_2$), 25.82 (*C*H$_2$), 22.74 (*C*H$_2$), 14.18 (*C*H$_3$).; *m/z* (ES^+) 699.4 $[M+Na]^+$ (2 x C18:2), 685.4 $[M+Na]^+$ (C18:1, C18:2), 671.5 $[M+Na]^+$ (2 x C18:1), 643.4 $[M+Na]^+$ (C18:2, C16:0), 629.4 $[M+Na]^+$ (C18:1, C16:0).

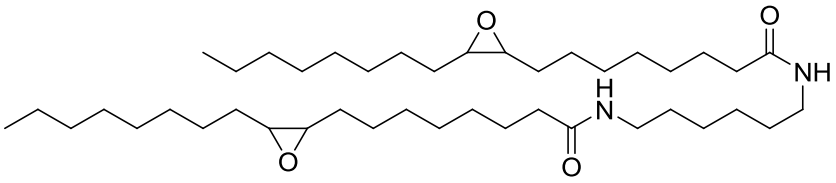
N,N'-(butane-1,4-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.58) (synthesised from soybean oil)



The general procedure for the epoxidation of difatty amides was applied using **3.50** (10.9 g, 18 mmol, 1.0 equiv.), and peracetic acid (15.1 mL, 89 mmol, 5.0 equiv.) to give product as a white solid (86 %); ν_{max}/cm^{-1} 3306 (N-H), 2921 (C-H), 2851 (C-H), 1633 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (s, 2H, N*H*), 3.35 – 3.18 (m, 4H, HNC*H*$_2$CH$_2$), 3.18 – 2.80 (m, 5H, *H*C(O)C*H*), 2.17 (t, *J* = 7.5 Hz, 4H,

O=CCH_2CH$_2$), 1.80 – 1.70 (m, 2H, (O)CHCH_2CH(O)), 1.62 (m, 4H, O=CCH$_2$CH_2), 1.53 (m, 16H, (O)CHCH_2, HNCH$_2$CH_2, CH_2), 1.29 (m, 28H, CH_2), 0.89 (dt, *J* = 13.0, 6.3 Hz, 6H, CH$_3$).; ^{13}C NMR (75 MHz, CDCl$_3$) δ 173.53 (O=*C*CH$_2$CH$_2$), 57.24 (H*C*(O)*C*H), 57.02 (H*C*(O)*C*H), 56.72 (H*C*(O)*C*H), 54.33 (H*C*(O)*C*H), 54.22 (H*C*(O)*C*H), 38.97 (HN*C*H$_2$CH$_2$), 36.61 (O=C*C*H$_2$CH$_2$), 31.88 (*C*H$_2$), 31.62 (*C*H$_2$), 29.66 (*C*H$_2$), 29.50 (*C*H$_2$), 29.32 (*C*H$_2$), 29.27 (*C*H$_2$), 27.83 (*C*H$_2$), 27.14 (O=CCH$_2$*C*H$_2$), 26.89 (*C*H$_2$), 26.59 (*C*H$_2$), 26.44 (*C*H$_2$), 26.20 (*C*H$_2$), 26.10 (*C*H$_2$), 25.74 (*C*H$_2$), 22.65 (*C*H$_2$), 22.53 (*C*H$_2$), 14.10 (*C*H$_3$), 13.97 (*C*H$_3$).; *m/z* (ES$^+$) 699.4 [M+Na]$^+$ (2 x C18:2), 685.4 [M+Na]$^+$ (C18:1, C18:2), 671.5 [M+Na]$^+$ (2 x C18:1), 643.4 [M+Na]$^+$ (C18:2, C16:0).

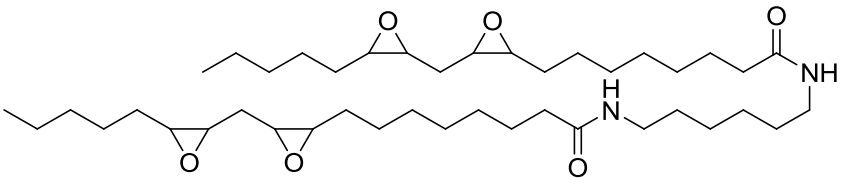
N,N'-(hexane-1,6-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.59)



The general procedure for the epoxidation of difatty amides was applied using **3.51** (18.5 g, 29 mmol, 1.0 equiv.), and peracetic acid (12.2 mL, 71 mmol, 2.5 equiv.) to give product as a white solid (98 %); ν_{max}/cm^{-1} 3303 (N-H), 2917 (C-H), 2850 (C-H), 1632 (C=O).; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.13 (t, *J* = 5.4 Hz, 2H, N*H*), 3.22 (dt, *J* = 6.5 Hz, 4H, HNCH_2CH$_2$CH$_2$), 2.90 (s, 4H, *H*C(O)C*H*), 2.17 (t, *J* = 7.5 Hz, 4H, O=CCH_2CH$_2$), 1.68 – 1.56 (m, 4H, O=CCH$_2$CH_2), 1.55 – 1.44 (m, 16H, (O)CHCH_2, HNCH$_2$CH_2CH$_2$, CH_2), 1.39 – 1.23 (m, 38H, HNCH$_2$CH$_2$CH_2, CH$_2$), 0.88 (t, *J* = 6.5 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, CDCl$_3$) δ 173.32 (O=*C*CH$_2$CH$_2$), 57.23 (H*C*(O)*C*H), 38.93 (HN*C*H$_2$CH$_2$CH$_2$), 36.70 (O=C*C*H$_2$CH$_2$), 31.84 (*C*H$_2$), 29.53 (*C*H$_2$), 29.37 (*C*H$_2$), 29.29 (*C*H$_2$), 29.21 (*C*H$_2$), 27.83 (*C*H$_2$), 27.79 (*C*H$_2$), 26.60

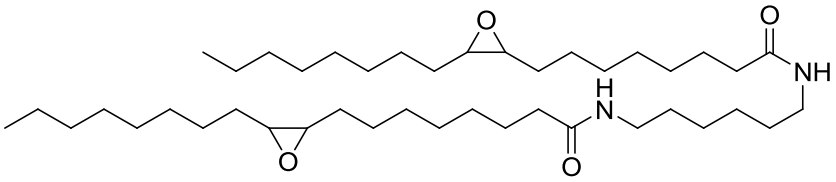
(CH_2), 26.06 (O=C$CH_2$$CH_2$), 25.80 ($CH_2$), 22.65 ($CH_2$), 14.10 ($CH_3$).; *m/z* ($ES^+$) 699.3 $[M+Na]^+$ (2 x C18:1).

N,N'-(hexane-1,6-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.60)



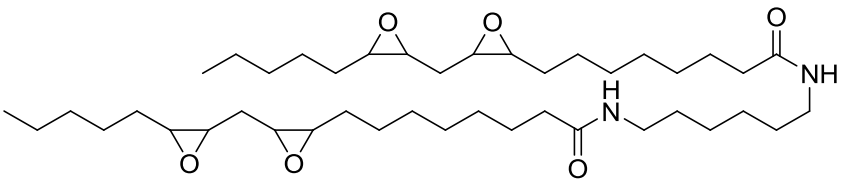
The general procedure for the epoxidation of difatty amides was applied using **3.52** (17.5 g, 27 mmol, 1.0 equiv.), and peracetic acid (23.0 mL, 136 mmol, 5.0 equiv.) to give product as a white solid (90 %); ν_{max}/cm^{-1} 3309 (N-H), 2918 (C-H), 2850 (C-H), 1632 (C=O).; ^1H NMR (300 MHz, $CDCl_3$) δ 6.09 (s, 2H, N*H*), 3.22 (dt, *J* = 12.9, 6.6 Hz, 4H, HNC$H_2$$CH_2$$CH_2$), 3.16 – 2.75 (m, 6H, *H*C(O)C*H*), 2.17 (t, *J* = 7.5 Hz, 4H, O=CC$H_2$$CH_2$), 1.80 – 1.68 (m, 2H, (O)CHCH_2CH(O)), 1.68 – 1.58 (m, 4H, O=CCH_2CH_2), 1.58 – 1.44 (m, 16H, (O)CHCH_2, HNCH_2C$H_2$$CH_2$, C$H_2$), 1.43 – 1.13 (m, 34H, HNC$H_2$$CH_2CH_2$, C$H_2$), 0.89 (dt, *J* = 6.8 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30 (O=*C*$CH_2$$CH_2$), 57.24 (H*C*(O)*C*H), 57.02 (H*C*(O)*C*H), 56.98 (H*C*(O)*C*H), 56.74 (H*C*(O)*C*H), 56.69 (H*C*(O)*C*H), 54.34 (H*C*(O)*C*H), 54.21 (H*C*(O)*C*H), 38.94 (HN*C*$H_2$$CH_2$$CH_2$), 36.69 (O=C*C*$H_2$$CH_2$), 31.89 ($CH_2$), 31.82 ($CH_2$), 31.64 ($CH_2$), 29.67 ($CH_2$), 29.51 ($CH_2$), 29.47 ($CH_2$), 29.30 ($CH_2$), 29.25 ($CH_2$), 29.19 ($CH_2$), 27.85 ($CH_2$), 27.78 ($CH_2$), 27.17 ($CH_2$), 26.91 ($CH_2$), 26.59 ($CH_2$), 26.45 ($CH_2$), 26.22 ($CH_2$), 26.12 ($CH_2$), 26.04 (O=C$CH_2$$CH_2$), 25.77 ($CH_2$), 22.64 ($CH_2$), 22.54 ($CH_2$), 14.10 ($CH_3$), 13.98 ($CH_3$).; *m/z* ($ES^+$) 727.5 $[M+Na]^+$ (2 x C18:2), 713.5 $[M+Na]^+$ (C18:1, C18:2), 699.5 $[M+Na]^+$ (2 x C18:1).

N,N'-(hexane-1,6-diyl)bis(8-(3-octyloxiran-2-yl)octanamide) (3.61) (synthesised from rapeseed oil)



The general procedure for the epoxidation of difatty amides was applied using **3.53** (14.55 g, 23 mmol, 1.0 equiv.), and peracetic acid (19.2 mL, 113 mmol, 5.0 equiv.) to give product as a white solid (90 %); ν_{max}/cm^{-1} 3307 (N-H), 2919 (C-H), 2851 (C-H), 1632 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (t, *J* = 5.4 Hz, 2H, N*H*), 3.22 (dt, *J* = 12.9, 6.6 Hz, 4H, HNCH_2CH_2CH_2), 3.17 – 2.78 (m, 4H, *H*C(O)C*H*), 2.16 (t, *J* = 7.5 Hz, 4H, O=CCH_2CH_2), 1.83 – 1.69 (m, 1H, (O)CHCH_2CH(O)), 1.69 – 1.57 (m, 4H, O=CCH$_2$CH_2), 1.57 – 1.42 (m, 16H, (O)CHCH_2, HNCH$_2$CH_2CH$_2$, CH_2), 1.42 – 1.14 (m, 38H, HNCH$_2$CH$_2$CH_2, CH_2), 0.88 (t, *J* = 6.7 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.32 (O=*C*CH$_2$CH$_2$), 57.34 (H*C*(O)*C*H), 57.13 (H*C*(O)*C*H), 57.09 (H*C*(O)*C*H), 56.79 (H*C*(O)*C*H), 54.45 (H*C*(O)*C*H), 54.30 (H*C*(O)*C*H), 39.03 (HN*C*H$_2$CH$_2$CH$_2$), 36.87 (O=C*C*H$_2$CH$_2$), 31.94 (*C*H$_2$), 31.75 (*C*H$_2$), 29.78 (*C*H$_2$), 29.62 (*C*H$_2$), 29.59 (*C*H$_2$), 29.45 (*C*H$_2$), 29.35 (*C*H$_2$), 29.30 (*C*H$_2$), 27.93 (*C*H$_2$), 27.89 (*C*H$_2$), 27.30 (*C*H$_2$), 27.02 (*C*H$_2$), 26.70 (*C*H$_2$), 26.23 (*C*H$_2$), 26.10 (O=CCH$_2$*C*H$_2$), 25.86 (*C*H$_2$), 22.74 (*C*H$_2$), 22.65 (*C*H$_2$), 14.19 (*C*H$_3$), 14.08 (*C*H$_3$).; *m/z* (ES^+) 727.5 $[M+Na]^+$ (2 x C18:2), 713.5 $[M+Na]^+$ (C18:1, C18:2), 699.5 $[M+Na]^+$ (2 x C18:1), 671.5 $[M+Na]^+$ (C18:2, C16:0), 657.5 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(hexane-1,6-diyl)bis(8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide) (3.62) (synthesised from soybean oil)



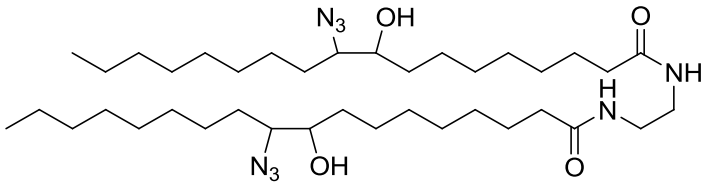
The general procedure for the epoxidation of difatty amides was applied using **3.54** (12.41 g, 19 mmol, 1.0 equiv.), and peracetic acid (16.4 mL, 96 mmol, 5.0 equiv.) to give product as a white solid (91 %); ν_{max}/cm^{-1} 3309 (N-H), 2918 (C-H), 2850 (C-H), 1632 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (s, 2H, N*H*), 3.23 (dd, *J* = 13.0, 6.6 Hz, 4H, HNC*H*$_2$CH$_2$CH$_2$), 3.17 – 2.81 (m, 6H, *H*C(O)C*H*), 2.16 (t, *J* = 7.5 Hz, 4H, O=CC*H*$_2$CH$_2$), 1.80 – 1.69 (m, 2H, (O)CHC*H*$_2$CH(O)), 1.67 – 1.58 (m, 4H, O=CC*H*$_2$CH$_2$), 1.57 – 1.42 (m, 16H, (O)CHC*H*$_2$, HNCH$_2$C*H*$_2$CH$_2$, C*H*$_2$), 1.40 – 1.22 (m, 34H, HNCH$_2$CH$_2$C*H*$_2$, C*H*$_2$), 0.89 (dt, *J* = 6.9 Hz, 6H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30 (O=*C*CH$_2$CH$_2$), 57.25 (H*C*(O)*C*H), 57.03 (H*C*(O)*C*H), 56.99 (H*C*(O)*C*H), 56.74 (H*C*(O)*C*H), 56.70 (H*C*(O)*C*H), 54.35 (H*C*(O)*C*H), 54.22 (H*C*(O)*C*H), 38.94 (HN*C*H$_2$CH$_2$CH$_2$), 36.70 (O=CCH$_2$CH$_2$), 31.90 (*C*H$_2$), 31.83 (*C*H$_2$), 31.65 (*C*H$_2$), 29.68 (*C*H$_2$), 29.47 (*C*H$_2$), 29.35 (*C*H$_2$), 27.86 (O=CCH$_2$*C*H$_2$), 27.18 (*C*H$_2$), 26.91 (*C*H$_2$), 26.60 (*C*H$_2$), 26.46 (*C*H$_2$), 26.23 (*C*H$_2$), 26.12 (*C*H$_2$), 26.04 (*C*H$_2$), 25.78 (*C*H$_2$), 22.67 (*C*H$_2$), 22.55 (*C*H$_2$), 14.11 (*C*H$_3$), 13.99 (*C*H$_3$).; *m/z* (ES$^+$) 727.5 $[M+Na]^+$ (2 x C18:2), 713.5 $[M+Na]^+$ (C18:1, C18:2), 699.5 $[M+Na]^+$ (2 x C18:1), 671.5 $[M+Na]^+$ (C18:2, C16:0), 657.5 $[M+Na]^+$ (C18:1, C16:0).

6.3.3 General Procedure for the azidation of difatty amides

The desired epoxy difatty amide (1 equiv.) was dissolved in ethanol:water (0.3 M, 5:1) and heated to 100 °C. Sodium azide (4 equiv. for oleic acid, 6 equiv. for linoleic acid, rapeseed oil and soybean oil) and ammonium chloride (4 equiv. for oleic acid, 6 equiv. for linoleic acid, rapeseed oil and soybean oil) was added and left to react at 100 °C overnight. The reaction mixture was diluted with water (200 mL)

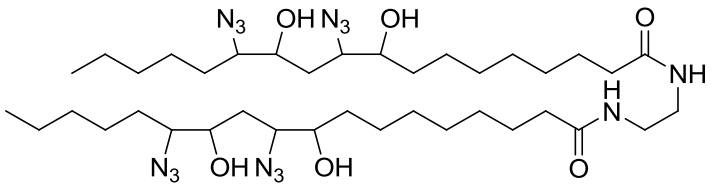
and extracted with chloroform. The organic layer was washed with saturated NaCl, separated and dried over $MgSO_4$. The solvent was removed in *vacuo* to produce pure product without further purification.

N,N'-(ethane-1,2-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.22)



The general procedure for the azidation of difatty amides was applied using **3.21** (12.6 g, 20 mmol, 1.0 equiv), sodium azide (5.3 g, 80 mmol, 4.0 equiv) and ammonium chloride (4.3 g, 80 mmol, 4.0 equiv.) to give the product as an orange solid. (92 %); ν_{max}/cm^{-1} 3350 (O-H), 3290 (N-H), 2921 (C-H), 2851 (C-H), 2100 ($N=N^+=N^-$), 1635 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.55 (s, 2H, N*H*), 3.68 – 3.46 (m, 2H, CH_2CH(OH)), 3.45 – 3.26 (m, 4H, $HNCH_2$), 3.18 (dt, *J* = 10.8, 5.0 Hz, 2H, $(N_3)CHCH_2$), 2.48 (br s, 2H, O*H*), 2.18 (t, *J* = 7.5 Hz, 4H, $O=CCH_2CH_2$), 1.74 – 1.56 (m, 8H, $(N_3)CHCH_2$, $O=CCH_2CH_2$), 1.55 – 1.41 (m, 8H, CH_2CH(OH), CH_2), 1.41 – 1.15 (m, 36H, CH_2), 0.88 (t, *J* = 6.4 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.80 ($O=CCH_2CH_2$), 73.62 (CH_2CH(OH)), 67.34 ($(N_3)CHCH_2$), 67.12 ($(N_3)CHCH_2$), 40.16 ($HNCH_2$), 36.68 ($O=CCH_2CH_2$), 34.39 (CH_2CH(OH)), 34.30 (CH_2CH(OH)), 31.97 (CH_2), 30.95 (CH_2), 30.86 ($(N_3)CHCH_2$), 29.72 (CH_2), 29.64 (CH_2), 29.59 (CH_2), 29.34 (CH_2), 29.18 (CH_2), 29.08 (CH_2), 26.42 (CH_2), 26.29 (CH_2), 25.83 (CH_2), 25.71 ($O=CCH_2CH_2$), 22.77 (CH_2), 14.22 (CH_3).; *m/z* (ES^+) 729.5 $[M+Na]^+$ (2 x C18:1).

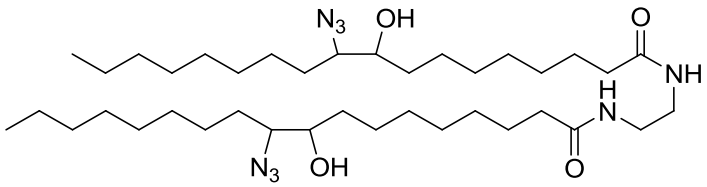
N,N'-(ethane-1,2-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.24)



The general procedure for the azidation of difatty amides was applied using **3.23** (11.9 g, 18 mmol, 1.0 equiv), sodium azide (7.2 g, 109 mmol, 6.0 equiv) and ammonium chloride (5.9 g, 109 mmol, 6.0 equiv.) to give the product as an orange solid. (88 %); ν_{max}/cm^{-1} 3350 (O-H), 3292 (N-H), 2922 (C-H), 2852 (C-H), 2100 ($N=N^+=N^-$), 1637 (C=O).; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.65 – 6.29 (m, 2H, N*H*), 4.05 – 3.46 (m, 4H, CH_2CH(OH), $(N_3)CHCH_2$), 3.44 – 3.27 (m, 4H, $HNCH_2$), 3.23 – 3.07 (m, 2H, $(N_3)CHCH_2$), 2.18 (t, *J* = 7.4 Hz, 4H, $O=CCH_2CH_2$), 1.72 – 1.53 (m, 10H, $O=CCH_2CH_2$, $(N_3)CHCH_2$, $(N_3)CHCH_2CH(OH)$), 1.52 – 1.00 (m, 40H, $CH_2CH(OH)$, CH_2), 0.89 (dt, *J* = 6.4 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.03 ($O=CCH_2CH_2$), 74.49 ($CH_2CH(OH)$), 73.63 ($CH_2CH(OH)$), 73.19 ($CH_2CH(OH)$), 72.82 ($CH_2CH(OH)$), 70.71 ($CH_2CH(OH)$), 70.37 ($CH_2CH(OH)$), 69.73 ($CH_2CH(OH)$), 67.51 ($(N_3)CHCH_2$), 67.33 ($(N_3)CHCH_2$), 67.12 ($(N_3)CHCH_2$), 66.66 ($(N_3)CHCH_2$), 64.47 ($(N_3)CHCH_2$), 64.22 ($(N_3)CHCH_2$), 63.74 ($(N_3)CHCH_2$), 39.99 ($HNCH_2$), 36.56 ($O=CCH_2CH_2$), 34.29 ($CH_2CH(OH)$), 31.96 (CH_2), 31.73 (CH_2), 30.86 ($(N_3)CHCH_2$), 30.59 (CH_2), 29.81 (CH_2), 29.59 (CH_2), 29.36 (CH_2), 29.10 (CH_2), 25.71 ($O=CCH_2CH_2$), 22.76 (CH_2), 22.69 (CH_2), 14.22 (CH_3), 14.14 (CH_3).; *m/z* (ES^+) 843.5 $[M+Na]^+$ (2 x C18:2), 786.5 $[M+Na]^+$ (C18:2, C18:1), 729.5 $[M+Na]^+$ (2 x C18:1).

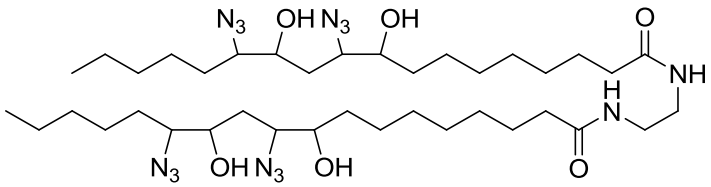
N,N'-(ethane-1,2-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.39)

(synthesised from rapeseed oil)



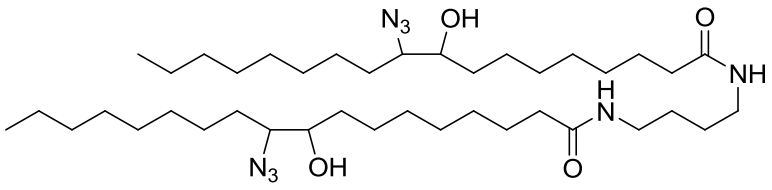
The general procedure for the azidation of difatty amides was applied using **3.37** (9.1 g, 14 mmol, 1.0 equiv), sodium azide (5.5 g, 84 mmol, 6.0 equiv) and ammonium chloride (4.5 g, 84 mmol, 6.0 equiv.) to give the product as an orange solid. (90 %); ν_{max}/cm^{-1} 3350 (O-H), 3292 (N-H), 2922 (C-H), 2852 (C-H), 2102 ($N=N^+=N^-$), 1636 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.75 (s, 2H, N*H*), 3.66 – 3.47 (m, 2H, $CH_2CH(OH)$), 3.42 – 3.27 (m, 4H, $HNCH_2$), 3.17 (dt, *J* = 9.9, 6.0 Hz, 2H, $(N_3)CHCH_2$), 2.18 (t, *J* = 7.3 Hz, 4H, $O=CCH_2CH_2$), 1.72 – 1.54 (m, 8H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.54 – 1.40 (m, 8H, $CH_2CH(OH)$, CH_2), 1.40 – 1.15 (m, 36H, CH_2), 0.88 (t, *J* = 6.3 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.87 ($O=CCH_2CH_2$), 74.49 ($CH_2CH(OH)$), 74.18 ($CH_2CH(OH)$), 73.58 ($CH_2CH(OH)$), 73.09 ($CH_2CH(OH)$), 72.76 ($CH_2CH(OH)$), 67.25 ($(N_3)CHCH_2$), 67.03 ($(N_3)CHCH_2$), 64.25 ($(N_3)CHCH_2$), 63.67 ($(N_3)CHCH_2$), 39.98 ($HNCH_2$), 36.59 ($O=CCH_2CH_2$), 34.32 ($CH_2CH(OH)$), 31.92 (CH_2), 31.69 (CH_2), 30.88 ($(N_3)CHCH_2$), 30.80 (CH_2), 29.77 (CH_2), 29.61 (CH_2), 29.55 (CH_2), 29.33 (CH_2), 29.16 (CH_2), 26.39 (CH_2), 25.81 (CH_2), 25.70 ($O=CCH_2CH_2$), 22.72 (CH_2), 14.18 (CH_3).; *m/z* (ES^+) 843.5 $[M+Na]^+$ (2 x C18:2), 786.5 $[M+Na]^+$ (C18:2, C18:1), 729.5 $[M+Na]^+$ (2 x C18:1), 644.4 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(ethane-1,2-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.40) (synthesised from soybean oil)



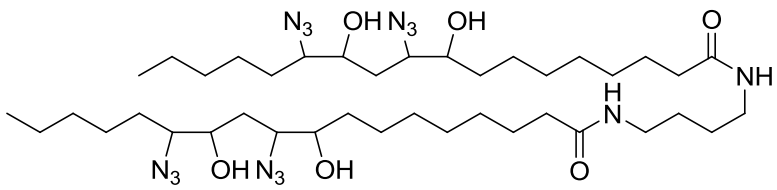
The general procedure for the azidation of difatty amides was applied using **3.38** (11.0 g, 17 mmol, 1.0 equiv), sodium azide (6.6 g, 101 mmol, 6.0 equiv) and ammonium chloride (5.4 g, 101 mmol, 6.0 equiv.) to give the product as an orange oil. (98 %); ν_{max}/cm^{-1} 3350 (O-H), 3296 (N-H), 2918 (C-H), 2850 (C-H), 2100 ($N=N^+=N^-$), 1637 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (s, 2H, N*H*), 4.01 – 3.48 (m, 4H, $CH_2CH(OH)$, $(N_3)CHCH_2$), 3.41 – 3.30 (m, 4H, $HNCH_2$), 3.27 – 3.04 (m, 2H, $(N_3)CHCH_2$), 2.18 (t, *J* = 7.0 Hz, 4H, $O=CCH_2CH_2$), 1.74 – 1.53 (m, 10H, $CH_2CH(OH)$, CH_2), 1.53 – 1.03 (m, 40H, CH_2), 0.90 (dt, *J* = 7.0 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.99 ($O=CCH_2CH_2$), 74.49 ($CH_2CH(OH)$), 73.87 ($CH_2CH(OH)$), 73.64 ($CH_2CH(OH)$), 73.17 ($CH_2CH(OH)$), 72.81 ($CH_2CH(OH)$), 70.71 ($CH_2CH(OH)$), 70.53 ($CH_2CH(OH)$), 70.38 ($CH_2CH(OH)$), 69.74 ($CH_2CH(OH)$), 67.79 ($(N_3)CHCH_2$), 67.64 ($(N_3)CHCH_2$), 67.53 ($(N_3)CHCH_2$), 67.34 ($(N_3)CHCH_2$), 67.12 ($(N_3)CHCH_2$), 66.79 ($(N_3)CHCH_2$), 63.73 ($(N_3)CHCH_2$), 40.02 ($HNCH_2$), 36.78 ($O=CCH_2CH_2$), 36.65 (CH_2), 36.56 (CH_2), 34.30 ($CH_2CH(OH)$), 32.03 (CH_2), 31.95 (CH_2), 31.85 (CH_2), 31.73 (CH_2), 30.96 (CH_2), 30.87 ($(N_3)CHCH_2$), 30.59 (CH_2), 29.81 (CH_2), 29.65 (CH_2), 29.47 (CH_2), 29.36 (CH_2), 29.17 (CH_2), 29.09 (CH_2), 28.94 (CH_2), 27.79 (CH_2), 26.41 (CH_2), 26.30 (CH_2), 25.86 (CH_2), 25.71 ($O=CCH_2CH_2$), 25.59 (CH_2), 22.77 (CH_2), 22.63 (CH_2), 14.22 (CH_3), 14.11 (CH_3).; *m/z* (ES^+) 843.5 $[M+Na]^+$ (2 x C18:2), 786.5 $[M+Na]^+$ (C18:2, C18:1), 729.5 $[M+Na]^+$ (2 x C18:1), 701.4 $[M+Na]^+$ (C18:2, C16:0), 644.4 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(butane-1,4-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.63)



The general procedure for the azidation of difatty amides was applied using **3.55** (12.6 g, 19 mmol, 1.0 equiv), sodium azide (5.1 g, 77 mmol, 4.0 equiv) and ammonium chloride (4.2 g, 77 mmol, 4.0 equiv.) to give the product as an orange solid. (88 %); ν_{max}/cm^{-1} 3350 (O-H), 3321 (N-H), 2927 (C-H), 2855 (C-H), 2103 ($N=N^+=N^-$), 1647 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.59 – 6.27 (m, 2H, N*H*), 3.73 – 3.46 (m, 2H, $CH_2CH(OH)$), 3.24 (dt, *J* = 6.7, 5.4 Hz, 4H, $HNCH_2CH_2$), 3.19 – 3.10 (m, 2H, $(N_3)CHCH_2$), 2.17 (t, *J* = 7.4 Hz, 4H, $O=CCH_2CH_2$), 1.74 – 1.56 (m, 8H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.52 (s, 12H, $CH_2CH(OH)$, $HNCH_2CH_2$, CH_2), 1.43 – 1.15 (m, 36H, CH_2), 0.88 (t, *J* = 6.4 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.76 ($O=CCH_2CH_2$), 73.84($CH_2CH(OH)$), 73.51 ($CH_2CH(OH)$), 67.19 ($(N_3)CHCH_2$), 66.99 ($(N_3)CHCH_2$), 39.01 ($HNCH_2CH_2$), 36.65 ($O=CCH_2CH_2$), 34.23 ($CH_2CH(OH)$), 34.17 ($CH_2CH(OH)$), 31.86 (CH_2), 30.79 (CH_2), 30.71 ($(N_3)CHCH_2$), 29.72 (CH_2), 29.65 (CH_2), 29.57 (CH_2), 29.50 (CH_2), 29.36 (CH_2), 29.29 (CH_2), 29.25 (CH_2), 29.16 (CH_2), 26.89 ($HNCH_2CH_2$), 26.36 (CH_2), 26.26 (CH_2), 25.76 ($O=CCH_2CH_2$), 25.62 (CH_2), 22.68 (CH_2), 14.13 (CH_3).; *m/z* (ES^+) 757.5 $[M+Na]^+$ (2 x C18:1).

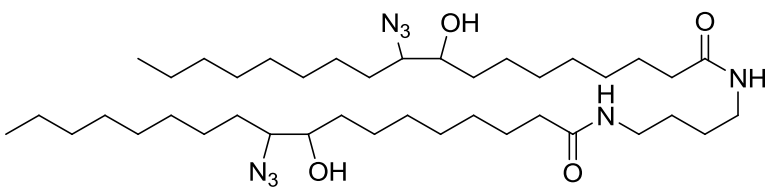
N,N'-(butane-1,4-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.64)



The general procedure for the azidation of difatty amides was applied using **3.56** (13.2 g, 19 mmol, 1.0 equiv), sodium azide (7.6 g, 116 mmol, 6.0 equiv) and ammonium chloride (6.2 g, 116 mmol, 6.0 equiv.) to give the product as an orange solid. (95 %); ν_{max}/cm^{-1} 3350 (O-H), 3300 (N-H), 2922 (C-H), 2853 (C-H), 2100 ($N=N^+=N^-$), 1632 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 – 5.89 (m, 2H, N*H*), 4.12 – 3.49 (m, 4H, CH_2CH(OH), (N_3)C*H*CH_2), 3.34 – 3.06 (m, 6H, HNC*H*$_2CH_2$, (N_3)C*H*CH_2), 2.18 (t, *J* = 7.3 Hz, 4H, O=CC*H*$_2CH_2$), 1.99 – 1.72 (m, 2H, (N_3)CHC*H*$_2$CH(OH)), 1.72 – 1.57 (m, 9H, O=CCH_2C*H*$_2$, (N_3)CHC*H*$_2$), 1.57 – 1.40 (m, 11H, C*H*$_2$CH(OH), HNCH_2C*H*$_2$, C*H*$_2$), 1.40 – 1.12 (m, 28H, C*H*$_2$), 0.86 (dt, *J* = 6.8, 5.2 Hz, 6H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.80 (O=*C*CH_2CH_2), 77.58 (CH_2*C*H(OH)), 77.16 (CH_2*C*H(OH)), 76.74 (CH_2*C*H(OH)), 74.52 (CH_2*C*H(OH)), 74.22 (CH_2*C*H(OH)), 73.93 (CH_2*C*H(OH)), 73.64 (CH_2*C*H(OH)), 70.38 ((N_3)*C*HCH_2), 69.82 ((N_3)*C*HCH_2), 67.52 ((N_3)*C*HCH_2), 67.38 ((N_3)*C*HCH_2), 67.17 (CH_2*C*H(OH)), 63.82 ((N_3)*C*HCH_2), 39.13 (HN*C*H_2CH_2), 36.82 (O=C*C*H_2CH_2), 34.40 (*C*H_2CH(OH)), 34.31 (*C*H_2CH(OH)), 31.97 (*C*H_2), 31.75 (*C*H_2), 30.89 ((N_3)CH*C*H_2), 30.58 (*C*H_2), 29.82 (*C*H_2), 29.59 (*C*H_2), 29.35 (*C*H_2), 29.21 (*C*H_2), 28.98 (*C*H_2), 26.98 (HNCH_2*C*H_2), 26.42 (*C*H_2), 26.04 (*C*H_2), 25.80 (O=CCH_2*C*H_2), 25.63 (*C*H_2), 22.78 (*C*H_2), 22.64 (*C*H_2), 14.24 (*C*H_3), 14.13 (*C*H_3).; *m/z* (ES^+) 871.5 $[M+Na]^+$ (2 x C18:2), 814.5 $[M+Na]^+$ (C18:2, C18:1), 757.5 $[M+Na]^+$ (2 x C18:1).

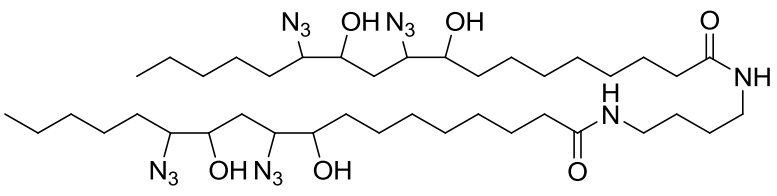
N,N'-(butane-1,4-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.65)

(synthesised from rapeseed oil)



The general procedure for the azidation of difatty amides was applied using **3.57** (13.8 g, 20 mmol, 1.0 equiv), sodium azide (7.9 g, 120 mmol, 6.0 equiv) and ammonium chloride (6.5 g, 120 mmol, 6.0 equiv.) to give the product as an orange solid. (86 %); ν_{max}/cm^{-1} 3350 (O-H), 3290 (N-H), 2921 (C-H), 2851 (C-H), 2100 ($N=N^+=N^-$), 1635 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 – 5.94 (m, 2H, N*H*), 3.68 – 3.47 (m, 2H, CH_2CH(OH)), 3.33 – 3.04 (m, 6H, $HNCH_2CH_2$, $(N_3)CHCH_2$), 2.17 (t, *J* = 7.3 Hz, 4H, $O=CCH_2CH_2$), 1.73 – 1.57 (m, 8H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.57 – 1.41 (m, 12H, CH_2CH(OH), $HNCH_2CH_2$, CH_2), 1.40 – 1.09 (m, 36H, CH_2), 0.88 (t, *J* = 6.6 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.79 ($O=CCH_2CH_2$), 73.62 (CH_2CH(OH)), 67.34 ($(N_3)CHCH_2$), 67.14 ($(N_3)CHCH_2$), 39.10 ($HNCH_2CH_2$), 36.78 ($O=CCH_2CH_2$), 34.36 (CH_2CH(OH)), 34.28 (CH_2CH(OH)), 32.02 (CH_2), 31.96 (CH_2), 31.72 (CH_2), 30.93 ($(N_3)CHCH_2$), 30.85 (CH_2), 29.80 (CH_2), 29.70 (CH_2), 29.63 (CH_2), 29.56 (CH_2), 29.46 (CH_2), 29.36 (CH_2), 29.26 (CH_2), 29.20 (CH_2), 29.14 (CH_2), 26.99 ($HNCH_2CH_2$), 26.41 (CH_2), 26.29 (CH_2), 25.94 (CH_2), 25.78 ($O=CCH_2CH_2$), 25.63 (CH_2), 22.75 (CH_2), 14.20 (CH_3).; *m/z* (ES^+) 871.5 $[M+Na]^+$ (2 x C18:2), 814.5 $[M+Na]^+$ (C18:2, C18:1), 757.5 $[M+Na]^+$ (2 x C18:1), 672.4 $[M+Na]^+$ (C18:1, C16:0).

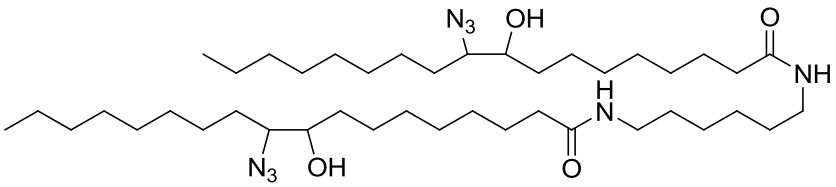
N,N'-(butane-1,4-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.66) (synthesised from soybean oil)



The general procedure for the azidation of difatty amides was applied using **3.58** (10.3 g, 15 mmol, 1.0 equiv), sodium azide (5.9 g, 90 mmol, 6.0 equiv) and

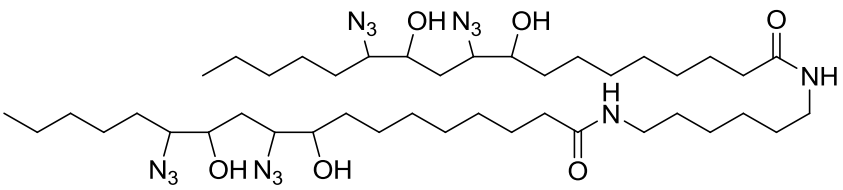
ammonium chloride (4.9 g, 90 mmol, 6.0 equiv.) to give the product as an orange solid. (89 %); ν_{max}/cm^{-1} 3350 (O-H), 3299 (N-H), 2918 (C-H), 2850 (C-H), 2099 ($N=N^+=N^-$), 1631 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 – 6.10 (m, 2H, N*H*), 4.02 – 3.48 (m, 4H, CH_2CH(OH), $(N_3)CHCH_2$), 3.31 – 3.04 (m, 6H, $HNCH_2CH_2$, $(N_3)CHCH_2$), 2.17 (t, *J* = 7.2 Hz, 4H, $O=CCH_2CH_2$), 1.99 – 1.71 (m, 2H, $(N_3)CHCH_2CH(OH)$), 1.71 – 1.56 (m, 9H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.56 – 1.37 (m, 11H, $CH_2CH(OH)$, $HNCH_2CH_2$, CH_2), 1.35 – 1.23 (m, 28H, CH_2), 0.89 (dt, *J* = 10.9, 6.7 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94 ($O=CCH_2CH_2$), 74.40 ($CH_2CH(OH)$), 74.17 ($CH_2CH(OH)$), 73.86 ($CH_2CH(OH)$), 73.60 ($CH_2CH(OH)$), 73.11 ($CH_2CH(OH)$), 72.82 ($CH_2CH(OH)$), 70.67 ($CH_2CH(OH)$), 70.54 ($CH_2CH(OH)$), 70.44 ($CH_2CH(OH)$), 70.37 ($CH_2CH(OH)$), 70.29 ($CH_2CH(OH)$), 69.85 ($(N_3)CHCH_2$), 67.72 ($(N_3)CHCH_2$), 67.58 ($(N_3)CHCH_2$), 67.45 ($(N_3)CHCH_2$), 67.29 ($(N_3)CHCH_2$), 67.17 ($(N_3)CHCH_2$), 67.08 ($(N_3)CHCH_2$), 67.00 ($(N_3)CHCH_2$), 66.89 ($(N_3)CHCH_2$), 66.65 ($(N_3)CHCH_2$), 64.24 ($(N_3)CHCH_2$), 63.73 ($(N_3)CHCH_2$), 39.11 ($HNCH_2CH_2$), 36.63 ($O=CCH_2CH_2$), 34.32 ($CH_2CH(OH)$), 34.24 ($CH_2CH(OH)$), 31.99 (CH_2), 31.93 (CH_2), 31.84 (CH_2), 31.70 (CH_2), 30.81 ($(N_3)CHCH_2$), 30.54 (CH_2), 30.38 (CH_2), 29.77 (CH_2), 29.73 (CH_2), 29.62 (CH_2), 29.54 (CH_2), 29.43 (CH_2), 29.33 (CH_2), 29.29 (CH_2), 29.18 (CH_2), 29.13 (CH_2), 29.02 (CH_2), 26.89 ($HNCH_2CH_2$), 26.39 (CH_2), 26.29 (CH_2), 26.02 (CH_2), 25.93 (CH_2), 25.79 ($O=CCH_2CH_2$), 25.69 (CH_2), 22.72 (CH_2), 22.66 (CH_2), 22.59 (CH_2), 14.19 (CH_3), 14.08 (CH_3).; *m/z* (ES^+) 871.5 $[M+Na]^+$ (2 x C18:2), 814.5 $[M+Na]^+$ (C18:2, C18:1), 757.5 $[M+Na]^+$ (2 x C18:1), 729.4 $[M+Na]^+$ (C18:2, C16:0), 672.4 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(hexane-1,6-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.67)



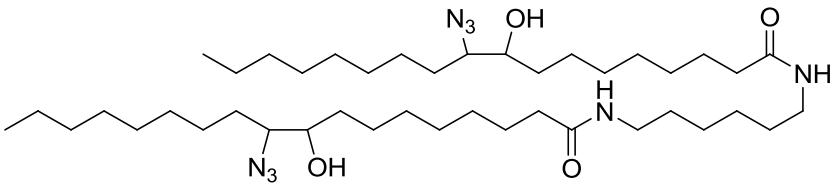
The general procedure for the azidation of difatty amides was applied using **3.59** (19.0 g, 28 mmol, 1.0 equiv), sodium azide (7.3 g, 112 mmol, 4.0 equiv) and ammonium chloride (6.0 g, 112 mmol, 4.0 equiv.) to give the product as an orange solid. (98 %); ν_{max}/cm^{-1} 3350 (O-H), 3303 (N-H), 2922 (C-H), 2852 (C-H), 2100 ($N=N^+=N^-$), 1631 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 5.96 (t, *J* = 5.5 Hz, 2H, N*H*), 3.58 – 3.50 (m, 1H, $CH_2CH(OH)$), 3.27 – 3.12 (m, 6H, $HNCH_2CH_2CH_2$, $(N_3)CHCH_2$), 2.16 (t, *J* = 7.5 Hz, 4H, $O=CCH_2CH_2$), 1.72 – 1.56 (m, 8H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.55 – 1.41 (m, 12H, $HNCH_2CH_2CH_2$, $CH_2CH(OH)$, CH_2), 1.40 – 1.17 (m, 40H, $HNCH_2CH_2CH_2$, CH_2), 0.88 (t, *J* = 6.6 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.52 ($O=CCH_2CH_2$), 73.58 ($CH_2CH(OH)$), 73.54 ($CH_2CH(OH)$), 67.26 ($(N_3)CHCH_2$), 67.11 ($(N_3)CHCH_2$), 39.03 ($HNCH_2CH_2CH_2$), 36.80 ($O=CCH_2CH_2$), 34.31 ($CH_2CH(OH)$), 34.25 ($CH_2CH(OH)$), 31.93 (CH_2), 31.91 (CH_2), 30.88 (CH_2), 30.81 (CH_2), 29.77 (CH_2), 29.68 (CH_2), 29.60 (CH_2), 29.53 (CH_2), 29.43 ($HNCH_2CH_2CH_2$), 29.33 (CH_2), 29.29 (CH_2), 29.20 (CH_2), 26.39 (CH_2), 26.29 (CH_2), 26.07 (CH_2), 25.80 (CH_2), 25.64 ($O=CCH_2CH_2$), 22.72 (CH_2), 14.18 (CH_3).; *m/z* (ES^+) 785.5 $[M+Na]^+$ (2 x C18:1).

N,N'-(hexane-1,6-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.68)



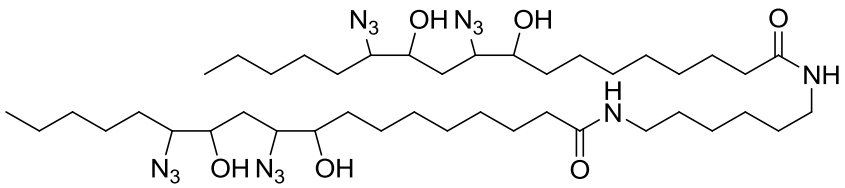
The general procedure for the azidation of difatty amides was applied using **3.60** (17.3 g, 24 mmol, 1.0 equiv), sodium azide (9.5 g, 144 mmol, 6.0 equiv) and ammonium chloride (7.9 g, 144 mmol, 6.0 equiv.) to give the product as an orange solid. (90 %); ν_{max}/cm^{-1} 3350 (O-H), 3303 (N-H), 2924 (C-H), 2854 (C-H), 2099 ($N=N^+=N^-$), 1632 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 – 5.86 (m, 2H N*H*), 3.99 – 3.50 (m, 4H, CH_2CH(OH), (N_3)C*H*CH_2), 3.29 – 3.06 (m, 6H, HNC*H*$_2CH_2CH_2$, (N_3)C*H*CH_2), 2.17 (t, *J* = 7.1 Hz, 4H, O=CC*H*$_2CH_2$), 1.98 – 1.71 (m, 2H, (N_3)CHC*H*$_2$CH(OH)), 1.70 – 1.56 (m, 9H, O=CCH_2C*H*$_2$, (N_3)CHC*H*$_2$), 1.56 – 1.39 (m, 11H, HNCH_2C*H*$_2CH_2$, C*H*$_2$CH(OH), C*H*$_2$), 1.38 – 1.20 (m, 32H, HNCH_2CH_2C*H*$_2$, C*H*$_2$), 0.99 – 0.82 (m, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.75 (O=*C*CH_2CH_2), 74.39 (CH_2*C*H(OH)), 74.16 (CH_2*C*H(OH)), 73.85 (CH_2*C*H(OH)), 73.56 (CH_2*C*H(OH)), 73.07 (CH_2*C*H(OH)), 72.80 (CH_2*C*H(OH)), 70.64 (CH_2*C*H(OH)), 70.52 (CH_2*C*H(OH)), 70.41 (CH_2*C*H(OH)), 70.29 (CH_2*C*H(OH)), 69.93 (CH_2*C*H(OH)), 67.72 ((N_3)*C*$CHCH_2$), 67.59 ((N_3)*C*$CHCH_2$), 67.42 ((N_3)*C*$CHCH_2$), 67.25 ((N_3)*C*$CHCH_2$), 67.16 ((N_3)*C*$CHCH_2$), 67.09 ((N_3)*C*$CHCH_2$), 66.99 ((N_3)*C*$CHCH_2$), 66.90 ((N_3)*C*$CHCH_2$), 66.74 ((N_3)*C*$CHCH_2$), 63.74 ((N_3)*C*$CHCH_2$), 39.08 (HN*C*$H_2CH_2CH_2$), 36.71 (O=C*C*H_2CH_2), 35.15 (*C*H_2), 34.31 (*C*H_2CH(OH)), 34.26 (*C*H_2CH(OH)), 31.93 (*C*H_2), 31.70 (*C*H_2), 30.82 (*C*H_2), 30.62 (*C*H_2), 30.54 (*C*H_2), 30.42 (*C*H_2), 30.17 (*C*H_2), 29.77 (*C*H_2), 29.49 (HNCH_2*C*H_2CH_2), 29.29 (*C*H_2), 29.20 (*C*H_2), 29.06 (*C*H_2), 26.39 (*C*H_2), 26.31 (*C*H_2), 26.07 (*C*H_2), 25.81 (*C*H_2), 25.74 (O=CCH_2*C*H_2), 22.72 (*C*H_2), 22.65 (*C*H_2), 22.59 (*C*H_2), 14.18 (*C*H_3), 14.08 (*C*H_3).; *m/z* (ES^+) 899.5 $[M+Na]^+$ (2 x C18:2), 842.5 $[M+Na]^+$ (C18:2, C18:1), 785.5 $[M+Na]^+$ (2 x C18:1).

N,N'-(hexane-1,6-diyl)bis(10-azido-9-hydroxyoctadecanamide) (3.69)



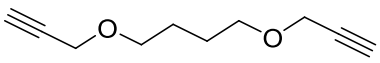
The general procedure for the azidation of difatty amides was applied using **3.61** (14.3 g, 20 mmol, 1.0 equiv), sodium azide (7.9 g, 120 mmol, 6.0 equiv) and ammonium chloride (6.5 g, 120 mmol, 6.0 equiv.) to give the product as an orange solid. (85 %); ν_{max}/cm^{-1} 3350 (O-H), 3303 (N-H), 2923 (C-H), 2853 (C-H), 2099 ($N=N^+=N^-$), 1642 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 – 5.88 (m, 2H, N*H*), 3.56 (m, 2H, $CH_2CH(OH)$), 3.26 – 3.12 (m, 6H, $HNCH_2CH_2CH_2$, $(N_3)CHCH_2$), 2.17 (t, *J* = 7.0 Hz, 4H, $O=CCH_2CH_2$), 1.67 – 1.57 (m, 8H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.55 – 1.40 (m, 12H, $CH_2CH(OH)$, $HNCH_2CH_2CH_2$, CH_2), 1.38 – 1.20 (m, 40H, CH_2, $HNCH_2CH_2CH_2$), 0.88 (t, *J* = 6.4 Hz, 6H, CH_2).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54 ($O=CCH_2CH_2$), 73.60 ($CH_2CH(OH)$), 73.56 ($CH_2CH(OH)$), 67.27 ($(N_3)CHCH_2$), 67.12 ($(N_3)CHCH_2$), 39.05 ($HNCH_2CH_2CH_2$), 36.81 ($O=CCH_2CH_2$), 34.33 ($CH_2CH(OH)$), 34.27 ($CH_2CH(OH)$), 31.92 (CH_2), 30.90 (CH_2), 30.84 (CH_2), 29.78 (CH_2), 29.69 (CH_2), 29.61 (CH_2), 29.54 (CH_2), 29.44 ($HNCH_2CH_2CH_2$), 29.34 (CH_2), 29.30 (CH_2), 29.21 (CH_2), 26.40 (CH_2), 26.31 (CH_2), 26.07 (CH_2), 25.82 (CH_2), 25.66 ($O=CCH_2CH_2$), 22.73 (CH_2), 14.19 (CH_3).; *m/z* (ES^+) 899.5 $[M+Na]^+$ (2 x C18:2), 842.5 $[M+Na]^+$ (C18:2, C18:1), 785.5 $[M+Na]^+$ (2 x C18:1), 757.5 $[M+Na]^+$ (C18:2, C16:0), 700.5 $[M+Na]^+$ (C18:1, C16:0).

N,N'-(hexane-1,6-diyl)bis(10,13-diazido-9,12-dihydroxyoctadecanamide) (3.70)



The general procedure for the azidation of difatty amides was applied using **3.62** (12.32 g, 17 mmol, 1.0 equiv), sodium azide (6.8 g, 102 mmol, 6.0 equiv) and ammonium chloride (5.6 g, 102 mmol, 6.0 equiv.) to give the product as an orange solid. (99 %); ν_{max}/cm^{-1} 3350 (O-H), 3303 (N-H), 2919 (C-H), 2852 (C-H), 2099 ($N=N^+=N^-$), 1632 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 – 5.84 (m, 2H, N*H*), 4.09 – 3.50 (m, 4H, CH_2CH(OH), $(N_3)CHCH_2$), 3.34 – 3.05 (m, 6H, $HNCH_2CH_2CH_2$, $(N_3)CHCH_2$), 2.17 (t, *J* = 6.5 Hz, 4H, $O=CCH_2CH_2$), 2.03 – 1.73 (m, 2H, $(N_3)CHCH_2CH$(OH)), 1.73 – 1.56 (m, 9H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.56 – 1.40 (m, 11H, $HNCH_2CH_2CH_2$, CH_2CH(OH), CH_2), 1.36 – 1.24 (m, 32H, $HNCH_2CH_2CH_2$, CH_2), 0.89 (dt, *J* = 11.8, 6.8 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.75 ($O=CCH_2CH_2$), 74.40 (CH_2CH(OH)), 74.16 (CH_2CH(OH)), 73.88 (CH_2CH(OH)), 73.60 (CH_2CH(OH)), 73.05 (CH_2CH(OH)), 70.64 (CH_2CH(OH)), 70.51 (CH_2CH(OH)), 70.40 (CH_2CH(OH)), 70.29 (CH_2CH(OH)), 69.90 (CH_2CH(OH)), 67.74 ($(N_3)CHCH_2$), 67.61 ($(N_3)CHCH_2$), 67.41 ($(N_3)CHCH_2$), 67.26 ($(N_3)CHCH_2$), 67.14 ($(N_3)CHCH_2$), 66.74 ($(N_3)CHCH_2$), 64.27 ($(N_3)CHCH_2$), 63.74 ($(N_3)CHCH_2$), 39.07 ($HNCH_2CH_2CH_2$), 36.72 ($O=CCH_2CH_2$), 34.32 (CH_2CH(OH)), 32.00 (CH_2), 31.92 (CH_2), 31.71 (CH_2), 30.89 (CH_2), 30.83 (CH_2), 30.54 (CH_2), 29.78 (CH_2), 29.62 (CH_2), 29.48 (CH_2), 29.44 ($HNCH_2CH_2CH_2$), 29.30 (CH_2), 29.20 (CH_2), 29.06 (CH_2), 26.30 (CH_2), 26.06 (CH_2), 25.96 (CH_2), 25.81 (CH_2), 25.74 ($O=CCH_2CH_2$), 22.74 (CH_2), 22.67 (CH_2), 22.60 (CH_2), 14.20 (CH_3), 14.09 (CH_3).; *m/z* (ES^+) 899.5 $[M+Na]^+$ (2 x C18:2), 842.5 $[M+Na]^+$ (C18:2, C18:1), 785.5 $[M+Na]^+$ (2 x C18:1), 757.5 $[M+Na]^+$ (C18:2, C16:0), 700.5 $[M+Na]^+$ (C18:1, C16:0).

6.3.4 Synthesis of 1,4-bis(prop-2-ynyloxy) butane linker (3.26)



1,4-Butandiol (20 g, 222 mmol, 1.0 equiv.) was dissolved in dry THF (400 mL, 0.5 M) under N_2. NaH (95 %) (19.5 g, 480 mmol, 2.2 equiv.) was added portion wise until effervescence had stopped. The reaction mixture was left under inert atmosphere for 30 mins. Propargyl bromide (80 wt. % in toluene) (54.4 mL, 480 mmol, 2.2 equiv.) was added dropwise and the reaction was left overnight. The mixture was neutralised by adding 2 M HCl dropwise until effervescence had stopped, diluted with water (100 mL), washed with saturated NaCl (100 mL) and dried over MgSO4. The solvent was removed *in vacuo.* to give crude product which was purified by silica plug (6:1 Hex:Et_2O) to give product as a yellow oil. (75 %) ν_{max}/cm^{-1} 3290 (C≡C), 2943 (C-H), 2858 (C-H), ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (d, *J* = 2.4 Hz, 4H, HC≡CC*H*$_2$), 3.54 (tt, *J* = 6.0, 3.7 Hz, 4H, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 2.45 (t, *J* = 2.4 Hz, 2H, *H*C≡CCH$_2$), 1.68 (tt, *J* = 6.1, 3.2 Hz, 4H, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O).; *m/z* (ES^+) 189.0 $[M+Na]^+$.

6.3.5 General Procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides

The desired azido fatty amide and 1,4-bis(prop-2-ynyloxy) butane linker (**3.26**) were dissolved in THF:H_2O (8:1) at room temperature. Copper sulfate and sodium ascorbate were dissolved in water in separate stock solutions. The required amount of copper sulfate and sodium ascorbate were combined and added to reaction which was left to react for 24 hours. The resultant polymer was then dried in 50 °C oven overnight.

P^{Cu}(C2-AzDOA) 3.31: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDOA **3.22** (0.5 g, 0.7 mmol,

1.0 equiv.), **3.26** (0.09 g, 0.6 mmol, 0.85 equiv.), $CuSO_4$ (0.018 g, 0.07 mmol, 0.1 equiv.) and sodium ascorbate (0.028 g, 0.14 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3301 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1645 (C=O), 1542 (C=C triazole), 1457 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br s, 2H, triazole NC*H*=C), 4.59 (br s, 4H, CCH_2O), 4.48 (br s, 2H, CH_2C*H*(triazole)), 3.89 (br s, 2H, (OH)C*H*CH_2), 3.51 (br s, 4H, $CCH_2OCH_2CH_2$), 3.34 (br m, 4H, HNCH_2), 2.13 (s, 4H, O=CCH_2CH_2), 2.03 (s, 4H, CH_2CH(triazole)), 1.64 (s, 4H, $CCH_2OCH_2CH_2$), 1.54 (s, 4H, O=CCH_2CH_2), 1.23 (br s, 44H, (OH)CHCH_2), CH_2), 0.86 (t, *J* = 6.8 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83 (O=*C*CH_2CH_2), 123.08 (triazole N*C*H=C), 72.41 ((HO)*C*HCH_2), 70.45 ($CCH_2OCH_2CH_2$), 66.06 (CH_2*C*H(triazole)), 64.38 (CCH_2O), 39.84 (HN*C*H_2) 36.54 (O=C*C*H_2CH_2), 31.98 (*C*H_2CH(triazole)), 29.65 (O=CCH_2*C*H_2), 29.49 (*C*H_2), 29.32 (*C*H_2), 28.95 (*C*H_2), 26.39 (*C*H_2), 26.14 (*C*H_2), 25.73 (CCH_2OCH_2*C*H_2), 22.75 (*C*H_2), 14.25 (*C*H_3).

P^{Cu}(C2-AzDLA) 3.32: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDLA **3.25** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.15 equiv.), $CuSO_4$ (0.018 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.026 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3301 (N-H, O-H), 2923 (C-H), 2853 (C-H), 1641 (C=O), 1543 (C=C triazole), 1455 (N=N triazole);

P^{Cu}(C2-AzDRSA) 3.41: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDRSA **3.39** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.), $CuSO_4$ (0.018 g, 0.07 mmol, 0.1 equiv.) and sodium ascorbate (0.028 g, 0.14 mmol, 0.2 equiv.) to give desired

polymer. ν_{max}/cm^{-1} 3300 (N-H, O-H), 2919 (C-H), 2851 (C-H), 1636 (C=O), 1541 (C=C triazole), 1457 (N=N triazole);

P^{Cu}(C2-AzDSBA) 3.42: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDSBA **3.40** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.10 equiv.), $CuSO_4$ (0.018 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.026 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3300 (N-H, O-H), 2921 (C-H), 2852 (C-H), 1639 (C=O), 1544 (C=C triazole), 1456 (N=N triazole);

P^{Cu}(C4-AzDOA) 3.71: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDOA **3.63** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.), $CuSO_4$ (0.017 g, 0.07 mmol, 0.1 equiv.) and sodium ascorbate (0.027 g, 0.14 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3304 (N-H, O-H), 2921 (C-H), 2853 (C-H), 1641 (C=O), 1543 (C=C triazole), 1460 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.65 (br m, 2H, triazole NC*H*=C), 4.73 – 4.53 (br m, 4H, CCH_2O), 4.53 – 4.40 (m, 2H, CH_2C*H*(triazole)), 3.94 – 3.82 (m, 2H, (OH)C*H*CH_2), 3.59 – 3.45 (m, 4H, CCH_2OC*H*$_2CH_2$), 3.30 – 3.12 (m, 4H, HNC*H*$_2CH_2$), 2.21 – 2.08 (m, 4H, O=CC*H*$_2CH_2$), 2.07 – 1.81 (m, 4H, C*H*$_2$CH(triazole)), 1.70 – 1.61 (m, 4H, CCH_2OCH_2C*H*$_2$), 1.58 – 1.46 (m, 8H, O=CCH_2C*H*$_2$, HNCH_2C*H*$_2$), 1.37 – 0.98 (m, *J* = 9.3 Hz, 46H, (OH)CHC*H*$_2$), CH_2), 0.86 (t, *J* = 6.3 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.02 (O=*C*CH_2CH_2), 122.96 (triazole N*C*H=C) 72.41 ((HO)*C*HCH_2), 70.40 ((HO)*C*HCH_2), 69.94 ((HO)*C*HCH_2), 66.02 (CH_2*C*H(triazole)), 64.39 (CC*H*$_2$O), 39.09 (HN*C*H_2), 36.59 (O=C*C*H_2CH_2), 32.24 (*C*H_2), 31.96 (*C*H_2CH(triazole)), 31.91 (*C*H_2), 29.63 (O=CCH_2*C*H_2), 29.47 (*C*H_2),

29.29 (*C*H_2), 28.97 (*C*H_2), 26.92 (*C*H_2), 26.37 (*C*H_2), 26.12 (*C*H_2), 25.80 ($CCH_2OCH_2CH_2$), 22.74 (*C*H_2), 14.23 (*C*H_3).

P^{Cu}(C4-AzDLA) 3.72: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDLA **3.64** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.13 g, 0.8 mmol, 1.3 equiv.), $CuSO_4$ (0.017 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.025 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3300 (N-H, O-H), 2921 (C-H), 2853 (C-H), 1638 (C=O), 1543 (C=C triazole), 1454 (N=N triazole);

P^{Cu}(C4-AzDRSA) 3.73: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDRSA **3.65** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.85 equiv.), $CuSO_4$ (0.016 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.025 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3300 (N-H, O-H), 2920 (C-H), 2852 (C-H), 1635 (C=O), 1541 (C=C triazole), 1457 (N=N triazole);

P^{Cu}(C4-AzDSBA) 3.74: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDSBA **3.66** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.15 equiv.), $CuSO_4$ (0.016 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.026 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3299 (N-H, O-H), 2920 (C-H), 2852 (C-H), 1635 (C=O), 1541 (C=C triazole), 1455 (N=N triazole);

P^{Cu}(C6-AzDOA) 3.75: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDOA **3.67** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.), $CuSO_4$ (0.013 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.021 g, 0.12 mmol, 0.2 equiv.) to give desired

polymer. ν_{max}/cm^{-1} 3303 (N-H, O-H), 2922 (C-H), 2852 (C-H), 1635 (C=O), 1542 (C=C triazole), 1458 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.63 (br m, 2H, triazole NC*H*=C), 4.73 – 4.54 (br m, 4H, CCH_2O), 4.54 – 4.38 (br m, 2H, CH_2C*H*(triazole)), 3.95 – 3.82 (br m, 2H, (OH)C*H*CH_2), 3.59 – 3.44 (br m, 4H, $CCH_2OCH_2CH_2$), 3.25 – 3.12 (br m, 4H, $HNCH_2CH_2CH_2$), 2.20 – 2.10 (br m, 4H, O=CCH_2CH_2), 2.10 – 1.96 (br m, 4H, CH_2CH(triazole)), 1.72 – 1.61 (br m, 4H, $CCH_2OCH_2CH_2$), 1.60 – 1.52 (br m, 4H O=CCH_2CH_2), 1.52 – 1.43 (br m, 4H, $HNCH_2CH_2CH_2$), 1.43 – 1.10 (br m, 48H, (OH)CHCH_2), CH_2), 0.86 (t, *J* = 6.8 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.68 (O=*C*CH_2CH_2), 122.87 (triazole N*C*H=C), 72.43 ((HO)*C*HCH_2), 70.40 ((HO)*C*HCH_2), 65.89 (CH_2*C*H(triazole)), 64.44 (CCH_2O), 39.12 (HN*C*H_2), 36.70 (O=C*C*H_2CH_2) 32.26 (*C*H_2), 31.97 (*C*H_2CH(triazole)), 31.92 (*C*H_2), 29.56 (O=CCH_2*C*H_2), 29.31 (*C*H_2), 29.09 (*C*H_2), 26.41 (*C*H_2), 26.15 (*C*H_2), 25.84 (CCH_2OCH_2*C*H_2), 22.75 (*C*H_2), 14.24 (*C*H_3).

P^{Cu}(C6-AzDLA) 3.76: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDLA **3.68** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.8 mmol, 1.25 equiv.), $CuSO_4$ (0.015 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.024 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3306 (N-H, O-H), 29219 (C-H), 2852 (C-H), 1634 (C=O), 1539 (C=C triazole), 1456 (N=N triazole);

P^{Cu}(C6-AzDRSA) 3.77: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDRSA **3.69** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.6 mmol, 0.9 equiv.), $CuSO_4$ (0.015 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.024 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3305 (N-H, O-H), 2920 (C-H), 2851 (C-H), 1634 (C=O), 1538 (C=C triazole), 1462 (N=N triazole);

P^{Cu}(C6-AzDSBA) 3.78: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDSBA **3.70** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.11 g, 0.8 mmol, 1.15 equiv.), $CuSO_4$ (0.015 g, 0.06 mmol, 0.1 equiv.) and sodium ascorbate (0.024 g, 0.12 mmol, 0.2 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3302 (N-H, O-H), 2918 (C-H), 2850 (C-H), 1633 (C=O), 1539 (C=C triazole), 1457 (N=N triazole);

6.3.6 General Procedure for Thermal 1,3 Huisgen cycloaddition of difatty amides

The desired azido fatty amide and 1,4-bis(prop-2-ynyloxy) butane linker (**3.26**) were dissolved in hot acetone and cast in 50 °C silicone mould. Acetone was evaporated in a 50 °C oven then the samples were transferred to 100 °C oven for 24 hours to give the required polymers

P^{T}(C2-AzDOA) 3.43: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDOA **3.22** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.6 mmol, 0.85 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3301 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1645 (C=O), 1543 (C=C triazole), 1458 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.45 (br m, 2H triazole NC*H*=C), 4.69 – 4.52 (br m, 4H, CCH_2O), 4.51 – 4.42 (br m, 2H, CH_2C*H*(triazole)), 3.97 – 3.83 (br m, 2H, (OH)C*H*CH_2), 3.62 – 3.42 (br m, 4H, $CCH_2OCH_2CH_2$), 3.41 – 3.20 (br m, 4H, HNCH_2), 2.21 – 2.07 (br m, 4H, O=CCH_2CH_2), 2.06 – 1.96 (br m, 4H, CH_2CH(triazole)), 1.71 – 1.43 (br m, 8H, $CCH_2OCH_2CH_2$, O=CCH_2CH_2), 1.42 – 0.92 (br m, 40H, (OH)CHCH_2), CH_2), 0.87 (t, *J* = 6.3 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.82 (O=*C*CH_2CH_2), 123.07 (triazole N*C*H=C), 72.40 ((HO)*C*HCH_2), 70.44 ((HO)*C*HCH_2), 68.09 ((HO)*C*HCH_2), 66.05 (CH_2*C*H(triazole)), 64.37 (CCH_2O), 39.83 (HN*C*H_2), 36.54 (O=C*C*H_2CH_2), 31.97

(*C*H_2CH(triazole)), 31.92 (*C*H_2), 29.65 (O=CCH_2*C*H_2), 29.48 (*C*H_2), 29.31 (*C*H_2), 28.94 (*C*H_2), 26.38 (*C*H_2), 26.13 (*C*H_2), 25.72 (CCH_2OCH_2*C*H_2), 22.74 (*C*H_2), 14.24 (*C*H_3).

P^T(C2-AzDLA) 3.44: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDLA **3.25** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.15 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3306 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1640 (C=O), 1541 (C=C triazole), 1456 (N=N triazole);

P^T(C2-AzDRSA) 3.45: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDRSA **3.39** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3301 (N-H, O-H), 2921 (C-H), 2852 (C-H), 1639 (C=O), 1544 (C=C triazole), 1458 (N=N triazole);

P^T(C2-AzDSBA) 3.46: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C2-AzDSBA **3.40** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.10 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3296 (N-H, O-H), 2922 (C-H), 2852 (C-H), 1640 (C=O), 1543 (C=C triazole), 1456 (N=N triazole);

P^T(C4-AzDOA) 3.79: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDOA **3.63** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3301 (N-H, O-H), 2922 (C-H), 2852 (C-H), 1633 (C=O), 1540 (C=C triazole), 1457 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.52 (m, 2H triazole NC*H*=C), 4.69 – 4.51 (m, 4H, CC*H*$_2$O), 4.52 – 4.44 (m, 2H, CH_2C*H*(triazole)), 3.96 – 3.84 (m,

2H, (OH)C*H*CH_2), 3.64 – 3.41 (m, 4H, $CCH_2OC\mathit{H}_2CH_2$), 3.31 – 3.13 (m, 4H, $HNC\mathit{H}_2CH_2$), 2.20 – 2.08 (m, 4H, $O{=}CC\mathit{H}_2CH_2$), 2.05 – 1.79 (m, 4H, $C\mathit{H}_2$CH(triazole)), 1.71 – 1.41 (m, 12H, $CCH_2OCH_2C\mathit{H}_2$, $O{=}CCH_2C\mathit{H}_2$, $HNCH_2C\mathit{H}_2$), 1.41 – 0.93 (m, 40H, (OH)CHCH_2), CH_2), 0.87 (t, *J* = 6.7 Hz, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.42 ($O{=}\mathit{C}CH_2CH_2$), 122.91 (triazole N*C*H=C), 72.42 ((HO)*C*HCH_2), 65.90 ($CH_2\mathit{C}$H(triazole)), 64.43 (CCH_2O), 39.14 (HN*C*H_2), 36.59 ($O{=}C\mathit{C}H_2CH_2$), 31.97 ($\mathit{C}H_2$CH(triazole)), 29.64 ($O{=}CCH_2\mathit{C}H_2$), 29.31 ($\mathit{C}H_2$), 25.86 ($CCH_2OCH_2\mathit{C}H_2$), 22.78 ($\mathit{C}H_2$), 14.24 ($\mathit{C}H_3$).

P^T(C4-AzDLA) 3.80: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDLA **3.64** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.13 g, 0.8 mmol, 1.3 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3304 (N-H, O-H), 2923 (C-H), 2853 (C-H), 1639 (C=O), 1543 (C=C triazole), 1454 (N=N triazole);

P^T(C4-AzDRSA) 3.81: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDRSA **3.65** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.85 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3297 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1640 (C=O), 1543 (C=C triazole), 1457 (N=N triazole);

P^T(C4-AzDSBA) 3.82: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C4-AzDSBA **3.66** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.7 mmol, 1.15 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3302 (N-H, O-H), 2921 (C-H), 2852 (C-H), 1639 (C=O), 1543 (C=C triazole), 1453 (N=N triazole);

P^{T}(C6-AzDOA) 3.83: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDOA **3.67** (0.5 g, 0.7 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.5 mmol, 0.80 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3305 (N-H, O-H), 2920 (C-H), 2852 (C-H), 1636 (C=O), 1542 (C=C triazole), 1457 (N=N triazole); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.51 (br m, 2H, triazole NC*H*=C), 4.66 – 4.53 (br m, 4H, CC*H*$_2$O), 4.51 – 4.27 (br m, 2H, CH$_2$C*H*(triazole)), 3.97 – 3.83 (br m, 2H, (OH)C*H*CH$_2$), 3.66 – 3.40 (br m, 4H, CCH$_2$OC*H*$_2$CH$_2$), 3.28 – 3.10 (br m, 4H, HNC*H*$_2$CH$_2$CH$_2$), 2.25 – 2.08 (br m, 4H, O=CC*H*$_2$CH$_2$), 2.06 – 1.73 (br m, 4H, C*H*$_2$CH(triazole)), 1.69 – 1.40 (br m, 12H, CCH$_2$OCH$_2$C*H*$_2$, O=CCH$_2$C*H*$_2$, HNCH$_2$C*H*$_2$CH$_2$), 1.39 – 0.93 (br m, 48H, (OH)CHC*H*$_2$, C*H*$_2$), 0.92 – 0.79 (br m, 6H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.74 (O=*C*CH$_2$CH$_2$), 133.87 (triazole N*C*H=C), 69.17 ((HO)*C*HCH$_2$), 69.11 ((HO)*C*HCH$_2$), 65.82 (CH$_2$*C*H(triazole)), 64.42 (CC*H*$_2$O), 39.10 (HN*C*H$_2$), 36.80 (O=C*C*H$_2$CH$_2$), 31.93 (*C*H$_2$CH(triazole)), 29.56 (O=CCH$_2$*C*H$_2$), 29.31 (*C*H$_2$), 26.41 (*C*H$_2$), 25.86 (CCH$_2$OCH$_2$*C*H$_2$), 22.76 (*C*H$_2$), 14.25 (*C*H$_3$).

P^{T}(C6-AzDLA) 3.84: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDLA **3.68** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.12 g, 0.8 mmol, 1.25 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3304 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1640 (C=O), 1543 (C=C triazole), 1458 (N=N triazole);

P^{T}(C6-AzDRSA) 3.85: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDRSA **3.69** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.09 g, 0.6 mmol, 0.9 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3305 (N-H, O-H), 2923 (C-H), 2853 (C-H), 1632 (C=O), 1538 (C=C triazole), 1462 (N=N triazole);

P^T(C6-AzDSBA) 3.86: The general procedure for the copper catalysed 1,3-Huisgen cycloaddition of difatty amides was applied using C6-AzDSBA **3.70** (0.5 g, 0.6 mmol, 1.0 equiv.), **3.26** (0.11 g, 0.8 mmol, 1.15 equiv.) to give desired polymer. ν_{max}/cm^{-1} 3305 (N-H, O-H), 2920 (C-H), 2852 (C-H), 1635 (C=O), 1541 (C=C triazole), 1457 (N=N triazole);

GPC analysis of the 6 soluble polymers shows the polymers made are low MWt short chain polymers and all have low polydispersities.

6.3.7 GPC Data for diamide polymers

Polymer	Mw	PD
P^{Cu}(C2-AzDOA) **3.31**	4239	1.10
P^{T}(C2-AzDOA) **3.43**	11549	1.04
P^{Cu}(C4-AzDOA) **3.71**	19131	1.02
P^{T}(C4-AzDOA) **3.79**	1781	1.14
P^{Cu}(C6-AzDOA) **3.75**	2807	1.13
P^{T}(C6-AzDOA) **3.83**	3691	1.06

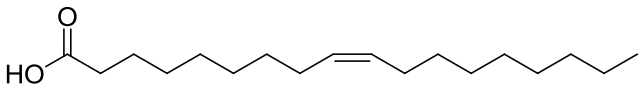
where: Mw = weight average MWt and PD = polydispersity

6.4 General Procedures in Chapter 4

6.4.1 General procedure for the synthesis of fatty acids from triglycerides

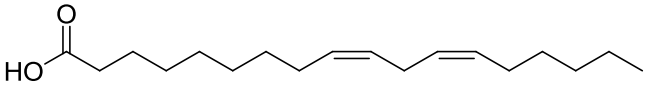
The desired triglyceride (1 equiv.) emulsified in water heated to 100 °C. NaOH was added and left to react for 48 hours. When complete by NMR the reaction was acidified with 2 M hydrochloric acid and allowed to cool to room temperature when the crude reaction mixture was dissolved in hexane. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo* to give the desired product. The product was used without further purification.

Oleic acid (Synthesised from rapeseed oil)



The general procedure for the synthesis of fatty acids from triglycerides was applied using rapeseed oil (100 g, 113 mmol, 1.0 equiv.), NaOH (27.2 g, 679 mmol, 6.0 equiv.) and water (1.25 L, 0.1 M). The reaction was dissolved in hexane (500 mL), dried over $MgSO_4$ to give a yellow oil (90 %); ν_{max}/cm^{-1} 2922 (C-H), 2853 (C-H), 1707 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) 5.47 – 5.20 (m, 2 H, *H*C=C*H*), 2.86 – 2.68 (m, 1 H, CH=CHC*H*$_2$CH=CH), 2.34 (t, 2 H, *J* 7.5, O=CC*H*$_2$CH$_2$), 2.14 – 1.91 (m 4 H, =CHC*H*$_2$), 1.70 – 1.54 (m, 2 H, O=CC*H*$_2$CH$_2$), 1.43 – 1.15 (m, 17 H, long chain C*H*$_2$), 0.97 (t, *J* 7.5, 1 H, =CHCH$_2$C*H*$_3$) 0.88 (t, *J* 6.6, 3 H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 179.96 (O=*C*CH$_2$), 131.23 – 126.47 (H*C*=*C*H), 33.50 (O=C*C*H$_2$), 31.32 (*C*H$_2$), 30.92 (*C*H$_2$), 29.16 (*C*H$_2$), 29.07 (*C*H$_2$), 28.94 (*C*H$_2$), 28.74 (*C*H$_2$), 28.55 (*C*H$_2$), 28.46 (*C*H$_2$), 28.44 (*C*H$_2$), 26.59 (*C*H$_2$), 26.53 (*C*H$_2$), 24.99 (*C*H$_2$), 24.03 (*C*H$_2$), 22.08 (*C*H$_2$), 21.97 (*C*H$_2$), 19.92 (*C*H$_2$), 13.46 (*C*H$_3$); *m/z* (ES$^+$) 321.0 [M+K]$^+$ (C18:1) 319.0 [M+K]$^+$ (C18:2).

Linoleic acid (synthesised from soybean oil)



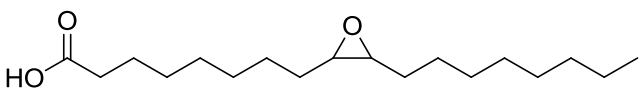
The general procedure for the synthesis of fatty acids from triglycerides was applied using soybean oil (100 g, 114 mmol, 1.0 equiv.), NaOH (27.4 g, 684 mmol, 6.0 equiv.) and water (1.25 L, 0.1 M). The reaction was dissolved in hexane (500 mL), dried over $MgSO_4$ to give a yellow oil (90 %); ν_{max}/cm^{-1} 2922 (C-H), 2853 (C-H), 1707 (C=O); ^{1}H NMR (300 MHz, CDCl3) δ 5.46 – 5.20 (m, 3H, *H*C=C*H*), 2.86 –

2.66 (m, 1H, HC=CHC*H*$_2$CH=CH), 2.34 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$), 2.10 – 1.94 (m, 4H, C*H*$_2$HC=CHC*H*$_2$), 1.75 – 1.55 (m, 2H, O=CCH$_2$C*H*$_2$), 1.46 – 1.17 (m, 17H, C*H*$_2$), 0.97 (t, *J* = 7.5 Hz, 1H, =CHCH$_2$C*H*$_3$), 0.87 (t, *J* = 6.9 Hz, 3H, C*H*3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.63 (O=*C*CH$_2$), 130.19 – 127.77 (H*C*=*C*H), 34.15 (O=C*C*H$_2$), 31.95 (*C*H$_2$), 31.56 (*C*H$_2$), 29.79 (*C*H$_2$), 29.70 (*C*H$_2$), 29.61 (*C*H$_2$), 29.56 (*C*H$_2$), 29.47 (*C*H$_2$), 29.38 (*C*H$_2$), 29.28 (*C*H$_2$), 29.18 (*C*H$_2$), 29.10 (*C*H$_2$), 29.06 (*C*H$_2$), 27.22 (*C*H$_2$), 25.64 (*C*H$_2$), 24.67 (*C*H$_2$), 22.72 (*C*H$_2$), 22.61 (*C*H$_2$), 14.28 (*C*H$_3$), 14.13 (*C*H$_3$), 14.08 (*C*H$_3$); *m/z* (ES$^+$) 321.0 $[M+K]^+$ (C18:1) 319.0 $[M+K]^+$ (C18:2).

6.4.2 General Procedure for the synthesis of epoxidised fatty acids

The desired fatty acid (1 equiv.) was dissolved in toluene at 60 °C, Amberlite® IR 120 (25 wt%), acetic acid (0.5 equiv) and H_2O_2 (4 equiv) were added and reacted overnight at 60 °C. Amberlite® was filtered off and reaction mixture was washed with water (2 x 200 mL) and the organic layer separated and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce pure product without further purification.

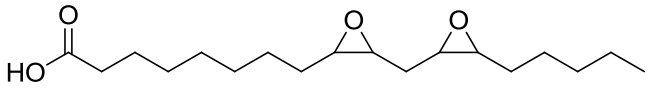
8-(3-octyloxiran-2-yl)octanoic acid



The general procedure for the synthesis of epoxidised fatty acids was applied using oleic acid (25 g, 89 mmol), Amberlite® IR 120 (6.75 g, 25 wt%), acetic acid (2.66 g, 44 mmol, 0.5 equiv.) and H_2O_2 (35 mL, 354 mmol, 4.0 equiv.), to give the product as a white solid. (87 %); ν_{max}/cm^{-1} 2914 (C-H), 2849 (C-H), 1692 (O=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 – 2.88 (m, 2H, *H*C(O)C*H*), 2.34 (t, *J* = 7.5 Hz, 2H,

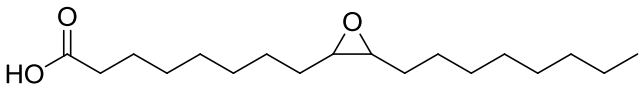
O=CCH_2), 1.68 – 1.58 (m, 2H, O=CCH$_2$CH_2), 1.56 – 1.46 (m, 4H, CH_2CH(O)CHCH_2), 1.45 – 1.24 (m, 20H, CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.85 (O=*C*CH$_2$), 57.47 (H*C*(O)*C*H), 57.42 (H*C*(O)*C*H), 34.13 (O=C*C*H$_2$), 31.96 (*C*H$_2$), 29.65 (*C*H$_2$), 29.42 (*C*H$_2$), 29.33 (*C*H$_2$), 29.27 (*C*H$_2$), 29.06 (*C*H$_2$), 27.89 (*C*H$_2$), 27.85 (*C*H$_2$), 26.69 (*C*H$_2$), 26.65 (*C*H$_2$), 24.74 (O=CCH$_2$*C*H$_2$), 22.77 (*C*H$_2$), 14.20 (*C*H$_3$); *m/z* (ES$^+$) 321.0 [M+Na]$^+$ (C18:1).

8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoic acid



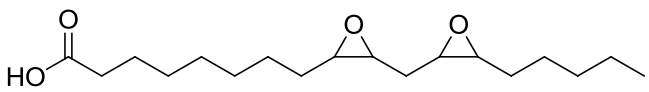
The general procedure for the synthesis of epoxidised fatty acids was applied using linoleic acid (25 g, 89 mmol, 1.0 equiv.), Amberlite® IR 120 (6.75 g, 25 wt%), acetic acid (2.7 g, 45 mmol) and H_2O_2 (35 mL, 357 mmol, 4.0 equiv.), to give the product as a white solid. (84 %); ν_{max}/cm^{-1} 2910 (C-H), 2849 (C-H), 1691 (O=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 – 2.89 (m, 4H, *H*C(O)C*H*), 2.34 (t, *J* = 7.4 Hz, 2H, O=CCH_2), 1.85 – 1.69 (m, 2H, HC(O)CHCH_2CH(O)CH), 1.68 – 1.58 (m, 2H O=CCH$_2$CH_2), 1.58 – 1.49 (m, 4H, CH_2CH(O)CH), 1.47 – 1.23 (m, 14H, CH_2), 0.90 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.57 (O=*C*CH$_2$), 57.19 (H*C*(O)*C*H), 57.13 (H*C*(O)*C*H), 56.90 (H*C*(O)*C*H), 56.83 (H*C*(O)*C*H), 54.50 (H*C*(O)*C*H), 54.34 (H*C*(O)*C*H), 34.06 (O=C*C*H$_2$), 31.73 (*C*H$_2$), 29.32 (*C*H$_2$), 29.20 (*C*H$_2$), 28.99 (*C*H$_2$), 27.91 (*C*H$_2$), 27.84 (*C*H$_2$), 27.22 (*C*H$_2$), 26.93 (*C*H$_2$), 26.57 (*C*H$_2$), 26.46 (*C*H$_2$), 26.30 (*C*H$_2$), 26.19 (*C*H$_2$), 24.69 (O=CCH$_2$*C*H$_2$), 22.63 (*C*H$_2$), 14.05 (*C*H$_3$); *m/z* (ES$^+$) 335.0 [M+Na]$^+$ (C18:2), 321.0 [M+Na]$^+$ (C18:1).

8-(3-octyloxiran-2-yl)octanoic acid (Synthesised from rapeseed oil)



The general procedure for the synthesis of epoxidised fatty acids was applied using hydrolysed rapeseed oil (25.0 g, 89 mmol), Amberlite® IR 120 (6.75 g, 25 wt%), acetic acid (2.7 g, 44 mmol, 0.5 equiv.) and H_2O_2 (35 mL, 355 mmol, 4.0 equiv), to give the product as a white solid. (83 %); ν_{max}/cm^{-1} 2913 (C-H) 2849 (C-H) 1692 (O=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 – 2.83 (m, 2H, *H*C(O)C*H*), 2.34 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$), 1.85 – 1.71 (m, 1H, HC(O)CHC*H*$_2$HC(O)CH), 1.69 – 1.58 (m, 2H, O=CCH$_2$C*H*$_2$), 1.56 – 1.44 (m, 4H, C*H*$_2$HC(O)CH), 1.44 – 1.17 (m, 17H C*H*$_2$), 1.06 (t, *J* = 7.5 Hz, 1H, (O)CHCH$_2$C*H*$_3$), 0.88 (t, *J* = 6.7 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, CDCl3) δ 179.84 (O=*C*CH$_2$), 57.36 (H*C*(O)*C*H), 57.31 (H*C*(O)*C*H), 57.11 (H*C*(O)*C*H), 57.05 (H*C*(O)*C*H), 56.82 (H*C*(O)*C*H), 56.74 (H*C*(O)*C*H), 54.42 (H*C*(O)*C*H), 54.25 (H*C*(O)*C*H), 34.01 (O=C*C*H$_2$), 31.83 (*C*H$_2$), 31.64 (*C*H$_2$), 29.66 (*C*H$_2$), 29.50 (*C*H$_2$), 29.28 (*C*H$_2$), 29.23 (*C*H$_2$), 29.19 (*C*H$_2$), 29.14 (*C*H$_2$), 28.93 (*C*H$_2$), 27.82 (*C*H$_2$), 27.74 (*C*H$_2$), 27.71 (*C*H$_2$), 26.55 (*C*H$_2$), 26.51 (*C*H$_2$), 24.67(O=CCH$_2$*C*H$_2$), 22.64 (*C*H$_2$), 14.07 (CH$_3$), 13.95 (CH$_3$).; *m/z* (ES$^+$) 335.0 [M+Na]$^+$ (C18:2), 321.0 [M+Na]$^+$ (C18:1).

8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanoic acid (Synthesised from soybean oil)



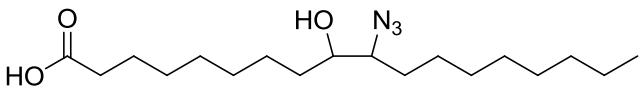
The general procedure for the synthesis of epoxidised fatty acids was applied using hydrolysed soybean oil (25.0 g, 89 mmol, 1.0 equiv.), Amberlite® IR 120 (6.75 g, 25

wt%), acetic acid (2.7 g, 45 mmol, 0.5 equiv.) and H_2O_2 (35 mL, 358 mmol, 4.0 equiv.), to give the product as a white solid. (86 %); ν_{max}/cm^{-1} 2912 (C-H), 2849 (C-H), 1693 (O=C); ^{1}H NMR (300 MHz, CDCl3) δ 3.23 – 2.84 (m, 3H, *H*C(O)C*H*), 2.34 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$), 1.82 – 1.71 (m, 1H, HC(O)CHC*H*$_2$HC(O)CH), 1.69 – 1.59 (m, 2H, O=CCH$_2$C*H*$_2$), 1.57 – 1.44 (m, 4H, C*H*$_2$HC(O)CH), 1.42 – 1.22 (m, 17H, C*H*$_2$), 1.06 (t, *J* = 7.5 Hz, 1H, (O)CHCH$_2$C*H*$_3$), 0.89 (t, *J* = 6.9 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.88 (O=*C*CH$_2$), 56.77 (H*C*(O)*C*H), 56.71 (H*C*(O)*C*H), 56.51 (H*C*(O)*C*H), 56.44 (H*C*(O)*C*H), 56.21 (H*C*(O)*C*H), 56.14 (H*C*(O)*C*H), 53.81 (H*C*(O)*C*H), 53.65 (H*C*(O)*C*H), 33.37 (O=C*C*H$_2$CH$_2$), 31.28 (*C*H$_2$), 31.21 (*C*H$_2$), 31.01 (*C*H$_2$), 29.04 (*C*H$_2$), 28.95 (*C*H$_2$), 28.88 (*C*H$_2$), 28.80 (*C*H$_2$), 28.72 (*C*H$_2$), 28.61 (*C*H$_2$), 28.49 (*C*H$_2$), 28.43 (*C*H$_2$), 28.29 (*C*H$_2$), 27.19 (*C*H$_2$), 27.11 (*C*H$_2$), 26.48 (*C*H$_2$), 26.20 (*C*H$_2$), 25.92 (*C*H$_2$), 25.88 (*C*H$_2$), 25.74 (*C*H$_2$), 25.58 (*C*H$_2$), 25.47 (*C*H$_2$), 23.98 (O=CCH$_2$*C*H$_2$), 22.02 (*C*H$_2$), 21.91 (*C*H$_2$), 14.52 (*C*H$_3$), 13.45 (*C*H$_3$); *m/z* (ES$^+$) 335.0 [M+Na]$^+$ (C18:2), 321.0 [M+Na]$^+$ (C18:1).

6.4.3 General Procedure for the synthesis of Azido fatty acids

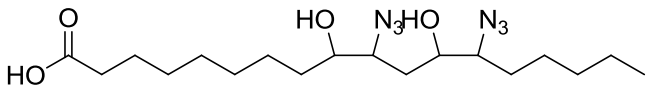
The desired epoxidised fatty acid (1 equiv.) was dissolved in ethanol:water (0.3 M, 5:1) at 100 °C. Sodium azide (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) and ammonium chloride (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) were added and reacted overnight at 100 °C. The reaction was diluted with water (200 mL) and extracted with chloroform. The organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce pure product without further purification.

10-Azido-9-hydroxyoctadecanoic acid (Oleic 4.12)



The general procedure for the synthesis of azido fatty acids was applied using epoxidised oleic acid (25.0 g, 84 mmol, 1.0 equiv), sodium azide (10.9 g, 168 mmol, 2.0 equiv) and ammonium chloride (9.0 g, 84 mmol, 2.0 equiv.) to give the product as an orange oil. (82 %); ν_{max}/cm^{-1} 3356 (O-H), 2922 (C-H), 2853, (C-H), 2099 ($N=N^+=N^-$), 1704 (C=O).; ^1H NMR (300 MHz, $CDCl_3$) δ 3.65 – 3.43 (m, 1H, $CH_2CH(OH)CH(N_3)CH_2$), 3.19 (dt, *J* = 6.6, 4.3 Hz, 1H, $CH_2CH(OH)CH(N_3)CH_2$), 2.30 (t, *J* = 6.3 Hz, 2H, $O=CCH_2$), 1.71 – 1.56 (m, 4H, $CH_2CH(OH)CH(N_3)CH_2$), 1.55 – 1.25 (m, 22H, $O=CCH_2CH_2$, CH_2), 0.88 (t, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.70 ($O=CCH_2$), 73.55 ($CH_2CH(OH)CH(N_3)CH_2$), 67.12 ($CH_2CH(OH)CH(N_3)CH_2$), 67.00 ($CH_2CH(OH)CH(N_3)CH_2$), 34.17 ($O=CCH_2$), 34.13 (CH_2), 31.82 (CH_2), 30.80 (CH_2), 29.57 (CH_2), 29.50 (CH_2), 29.44 (CH_2), 29.35 (CH_2), 29.24 (CH_2), 29.20 (CH_2), 29.12 (CH_2), 29.00 (CH_2), 26.26 (CH_2), 26.22 (CH_2), 25.64 (CH_2), 25.58 (CH_2), 24.85 (CH_2), 22.63 (CH_2), 14.07 (CH_3) ; *m/z* (ES^+) 364.1 $[M+Na]^+$ (C18:1).

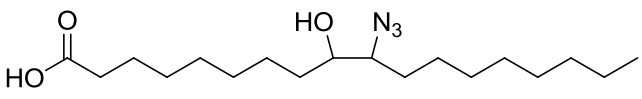
10,13-Diazido-9,12-dihydroxyoctadecanoic acid (Linoleic 4.12)



The general procedure for the synthesis of azido fatty acids was applied using epoxidised linoleic acid (25.0 g, 80 mmol, 1.0 equiv.), sodium azide (15.8 g, 241 mmol, 3.0 equiv.) and ammonium chloride (13.0 g, 241 mmol, 3.0 equiv.) to give the product as a brown viscous oil. (71 %); ν_{max}/cm^{-1} 3321 (O-H), 2922 (C-H), 2852, (C-

H), 2100 ($N=N^+=N^-$), 1706 (C=O).; ^{1}H NMR (300 MHz, CDCl3) δ 3.99 – 3.54 (m, 1.5H, $CH_2CH(OH)CH(N_3)CH_2$), 3.51 – 3.02 (m, 1.5H, $CH_2CH(OH)CH(N_3)CH_2$), 2.27 (t, *J* = 6.9 Hz, 2H, $O=CCH_2$), 2.03 – 1.20 (m, 22H, $O=CCH_2CH_2$, $CH_2CH(OH)$, $(N_3)CHCH_2$, $CH(N_3)CH_2CH(OH)$), 0.86 (t, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.88 ($O=CCH_2$), 73.84 ($CH_2CH(OH)$), 73.76 ($CH_2CH(OH)$), 73.11 ($CH_2CH(OH)$), 73.02 ($CH_2CH(OH)$), 72.61 ($CH_2CH(OH)$), 72.52 ($CH_2CH(OH)$), 69.94 ($CH_2CH(OH)$), 69.87 ($CH_2CH(OH)$), 69.79 ($CH_2CH(OH)$), 69.72 ($CH_2CH(OH)$), 69.61 ($CH_2CH(OH)$), 69.40 ($CH_2CH(OH)$), 67.02 ($CH(N_3)CH_2$), 66.79 ($CH(N_3)CH_2$), 66.65 ($CH(N_3)CH_2$), 66.30 ($CH(N_3)CH_2$), 66.21 ($CH(N_3)CH_2$), 66.14 ($CH(N_3)CH_2$), 63.63 ($CH(N_3)CH_2$), 63.54 ($CH(N_3)CH_2$), 63.45 ($CH(N_3)CH_2$), 63.06 ($CH(N_3)CH_2$), 62.91 ($CH(N_3)CH_2$), 62.65 ($CH(N_3)CH_2$), 37.35 ($O=CCH_2CH_2$), 35.61 (CH_2), 34.81 (CH_2), 34.55 (CH_2), 33.69 (CH_2), 33.36 (CH_2), 32.49 (CH_2), 32.17 (CH_2), 31.19 (CH_2), 31.06 (CH_2), 30.97 (CH_2), 30.13 (CH_2), 30.05 (CH_2), 29.89 (CH_2), 29.55 (CH_2), 29.45 (CH_2), 29.18 (CH_2), 28.43 (CH_2), 28.34 (CH_2), 28.26 (CH_2), 25.44 (CH_2), 25.33 (CH_2), 25.24 (CH_2), 24.91 (CH_2), 24.77 (CH_2), 24.10 (CH_2), 21.92 (CH_2), 21.87 (CH_2), 13.35 (CH_3); *m/z* (ES^+) 421.0 $[M+Na]^+$ (C18:2), 364.1 $[M+Na]^+$ (C18:1).

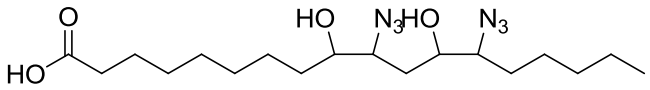
10-Azido-9-hydroxyoctadecanoic acid (RSO 4.12) (Synthesised from rapeseed oil)



The general procedure for the synthesis of azido fatty acids was applied using epoxidised hydrolysed rapeseed oil (22.0 g, 70 mmol, 1.0 equiv.), sodium azide (13.7 g, 211 mmol, 3.0 equiv.) and ammonium chloride (11.3 g, 211 mmol, 3.0 equiv.) to give the product as an orange viscous oil. (72 %); ν_{max}/cm^{-1} 3357 (O-H),

2923 (C-H), 2853, (C-H), 2099 ($N=N^+=N^-$), 1706 (C=O).; ^{1}H NMR (400 MHz, CDCl3) δ 3.95 – 3.47 (m, 1H, $CH_2CH(OH)CH(N_3)CH_2$), 3.42 – 3.06 (m, 1H, $CH_2CH(OH)CH(N_3)CH_2$), 2.43 – 2.13 (m, 2H, $O=CCH_2$), 1.78 – 1.53 (m, 4H, $(N_3)CHCH_2$, $O=CCH_2CH_2$), 1.51 – 0.97 (m, 22H, $CH_2CH(OH)$, $CH(N_3)CH_2CH(OH)$, $(N_3)CHCH_2CH_3$, CH_2), 0.88 (t, J = 6.6 Hz, 3H, CH_3).; ^{13}C NMR (101 MHz, CDCl3) δ 178.98 ($O=CCH_2$), 73.61 ($CH_2CH(OH)$), 67.23 ($(N_3)CHCH_2$), 67.09 ($(N3)CHCH_2$), 34.28 ($O=CCH_2$), 31.94 (CH_2), 31.87 (CH_2), 31.86 (CH_2), 30.89 (CH_2), 29.73 (CH_2), 29.61 (CH_2), 29.54 (CH_2), 29.50 (CH_2), 29.38 (CH_2), 29.27 (CH_2), 29.24 (CH_2), 29.05 (CH_2), 26.30 (CH_2), 25.69 (CH_2), 24.90 (CH_2), 22.67 (CH_2), 22.53 (CH_2), 14.11 (CH_3), 14.00 (CH_3); *m/z* (ES^+) 421.0 $[M+Na]^+$ (C18:2), 364.1 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxyoctadecanoic acid (SBO 4.12) (Synthesised from soybean oil)



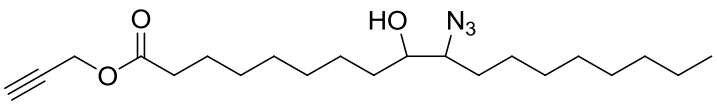
The general procedure for the synthesis of azido fatty acids was applied using epoxidised hydrolysed soybean oil (22.0 g, 71 mmol, 1.0 equiv.), sodium azide (13.8 g, 212 mmol, 3.0 equiv.) and ammonium chloride (11.3 g, 212 mmol, 3 equiv.) to give the product as a brown viscous oil. (84 %); ν_{max}/cm^{-1} 3322 (O-H), 2922 (C-H), 2852, (C-H), 2100 ($N=N^+=N^-$), 1706 (C=O).; ^{1}H NMR (300 MHz, CDCl3) δ 4.01 – 3.58 (m, 1.5H, $CH_2CH(OH)$), 3.57 – 3.09 (m, 1.5H, $(N_3)CHCH_2$), 2.33 (t, J = 7.1 Hz, 2H, $O=CCH_2$), 1.82 – 1.54 (m, 4H, $(N_3)CHCH_2$, $O=CCH_2CH_2$), 1.54 – 1.14 (m, 21H, $CH_2CH(OH)$, CH_2, $CH(N_3)CH_2CH(OH)$, $(N_3)CHCH_2CH_3$), 0.88 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl3) δ 179.86 ($O=CCH_2$), 73.60 ($CH_2CH(OH)$), 73.22 ($CH_2CH(OH)$), 73.11 ($CH_2CH(OH)$), 70.29 ($CH_2CH(OH)$), 69.99

($CH_2CH(OH)$), 67.72 ($(N_3)CHCH_2$), 67.36 ($(N_3)CHCH_2$), 67.18 ($(N_3)CHCH_2$), 67.07 ($(N_3)CHCH_2$), 66.90 ($(N_3)CHCH_2$), 64.18 ($(N_3)CHCH_2$), 63.70 ($(N_3)CHCH_2$), 63.56 ($(N_3)CHCH_2$), 34.25 ($O=CCH_2$), 31.94 (CH_2), 31.86 (CH_2), 31.62 (CH_2), 30.89 (CH_2), 30.61 (CH_2), 29.71 (CH_2), 29.49 (CH_2), 29.37 (CH_2), 29.27 (CH_2), 29.14 (CH_2), 28.96 (CH_2), 26.27 (CH_2), 25.89 (CH_2), 25.66 (CH_2), 25.44 (CH_2), 24.72 (CH_2), 22.67 (CH_2), 22.57 (CH_2), 22.52 (CH_2), 14.12 (CH_3), 14.00 (CH_3); *m/z* (ES^+) 421.0 $[M+Na]^+$ (C18:2), 364.1 $[M+Na]^+$ (C18:1).

6.4.4 General Procedure for the synthesis of azido propargyl fatty esters

The desired azido fatty acid (1 equiv.) was dissolved in DMF (0.25 M) at 50 °C, K_2CO_3 (2 equiv.) and propargyl bromide (80 wt. % in toluene) (1.5 equiv.) were added and reacted overnight at 50 °C. The reaction mixture was diluted with water (200 mL) and extracted with chloroform. The organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* and purification was achieved through silica plug (4:1 pet ether: ethyl acetate) to give pure product.

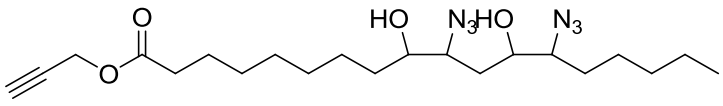
Prop-2-ynyl 10-azido-9-hydroxyoctadecanoate (OE 4.7)



The general procedure for the synthesis of azido propargyl fatty esters was applied using **oleic 4.12** (25.0 g, 73 mmol, 1.0 equiv.), K_2CO_3 (20.2 g, 146 mmol, 2.0 equiv.) and propargyl bromide (11.83 mL, 110 mmol, 1.5 equiv.) to give the product as a pale yellow oil. (65 %); ν_{max}/cm^{-1} 3440 (O-H), 3309 (≡C-H), 2924 (C-H), 2854 (C-H), 2100 ($-N_3$), 1739 (O=C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.4 Hz, 2H, $HC\equiv CCH_2O$), 3.53 (p, *J* = 6.5 Hz, 1H, $CH_2CH(OH)$), 3.20 (dt, *J* = 6.6 Hz, 1H,

(N_3)C*H*CH_2), 2.47 (t, *J* = 2.5 Hz, 1H, *H*C≡CCH_2O), 2.36 (td, *J* = 7.5, 1.9 Hz, 2H, O=CC*H*$_2$), 1.72 – 1.56 (m, 4H, O=CCH_2C*H*$_2$, (N_3)CHC*H*$_2$), 1.56 – 1.39 (m, 2H, C*H*$_2$CH(OH)), 1.39 – 1.20 (m, 20H, C*H*$_2$), 0.88 (t, *J* = 6.6 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.98 (O=*C*CH_2), 77.84 (H*C*≡CCH_2O), 74.76 (HC≡*C*CH_2O), 73.60 (CH_2*C*H(OH)), 73.53 (CH_2*C*H(OH)), 67.28 ((N_3)*C*HCH_2), 67.21 ((N_3)*C*HCH_2), 51.81 (HC≡C*C*H_2O), 34.37 (O=C*C*H_2), 34.30 (O=C*C*H_2), 33.98 (O=C*C*H_2), 31.87 (*C*H_2CH(OH)), 30.95 (O=CCH_2*C*H_2), 30.91 (O=CCH_2*C*H_2), 29.61 (*C*H_2), 29.55 (*C*H_2), 29.51 (*C*H_2), 29.35 (*C*H_2), 29.28 (*C*H_2), 29.13 (*C*H_2), 29.08 (*C*H_2), 28.95 (*C*H_2), 26.28 (*C*H_2), 26.20 (*C*H_2), 25.66 (*C*H_2), 25.56 (*C*H_2), 24.77 ((N_3)CH*C*H_2), 22.69 (*C*H_2), 14.14 (*C*H_3); *m/z* (ES^+) [M+Na^+] 402.3 (C18:1).

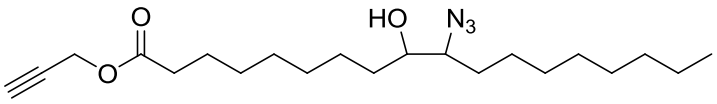
Prop-2-ynyl 10,13-diazido-9,12-dihydroxyoctadecanoate (LE 4.7)



The general procedure for the synthesis of azido propargyl fatty esters was applied using **linoleic 4.12** (20 g, 50 mmol, 1.0 equiv.), K_2CO_3 (13.9 g, 100 mmol, 2.0 equiv.) and propargyl bromide (8.1 mL, 75 mmol, 1.5 equiv.) to give the product as a pale yellow oil. (63 %); ν_{max}/cm^{-1}3440 (O-H), 3309 (≡C-H), 2926 (C-H), 2855 (C-H), 2101 (-N_3), 1735 (O=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.1 Hz, 2H, HC≡CC*H*$_2$O), 3.92 – 3.44 (m, 1.5H, CH_2C*H*(OH)), 3.43 – 3.12 (m, 1.5H, (N_3)C*H*CH_2), 2.48 (t, *J* = 2.2 Hz, 1H, *H*C≡CCH_2O), 2.36 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2$), 1.84 – 1.21 (m, 22H, O=CCH_2C*H*$_2$, C*H*$_2$CH(OH), (N_3)CHC*H*$_2$, CH(N_3)C*H*$_2$CH(OH)), 0.89 (t, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.10 (O=*C*CH_2), 77.89 (H*C*≡CCH_2O), 74.88 (HC≡*C*CH_2O), 73.90 (CH_2*C*H(OH)), 73.68 (CH_2*C*H(OH)), 73.60 (CH_2*C*H(OH)), 73.33 (CH_2*C*H(OH)), 73.19

($CH_2CH(OH)$), 72.69 ($CH_2CH(OH)$), 70.54 ($CH_2CH(OH)$), 70.45 ($CH_2CH(OH)$), 70.45 ($CH_2CH(OH)$), 67.92 ($(N_3)CHCH_2$), 67.61 ($(N_3)CHCH_2$), 67.54 ($(N_3)CHCH_2$), 67.33 ($(N_3)CHCH_2$), 67.26 ($(N_3)CHCH_2$), 67.04 ($(N_3)CHCH_2$), 63.95 ($(N_3)CHCH_2$), 63.80 ($(N_3)CHCH_2$), 63.30 ($(N_3)CHCH_2$), 51.91 ($HC{\equiv}CCH_2O$), 34.42 ($O{=}CCH_2$), 34.35 ($O{=}CCH_2$), 34.04 ($O{=}CCH_2$), 31.96 ($CH_2CH(OH)$), 31.72 ($CH_2CH(OH)$), 30.97 (CH_2), 30.90 (CH_2), 30.63 (CH_2), 29.80 (CH_2), 29.69 (CH_2), 29.55 (CH_2), 29.33 (CH_2), 29.28 (CH_2), 29.15 (CH_2), 29.03 (CH_2), 28.97 (CH_2), 26.28 (CH_2), 26.02 (CH_2), 25.93 (CH_2), 25.64 (CH_2), 24.84 ($(N_3)CHCH_2$), 22.77 (CH_2), 22.62 (CH_2), 14.23 (CH_3), 14.10 (CH_3).; *m/z* (ES^+) [$M+Na^+$] 459.3 (C18:2), [$M+Na^+$] 402.3 (C18:1).

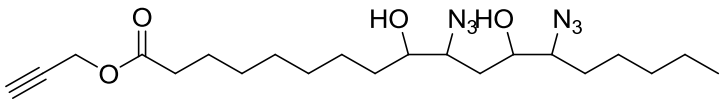
Prop-2-ynyl 10-azido-9-hydroxyoctadecanoate (RSE 4.7) (Synthesised from rapeseed oil)



The general procedure for the synthesis of azido propargyl fatty esters was applied using **RSO 4.12** (23.0 g, 57 mmol, 1.0 equiv.), K_2CO_3 (15.9 g, 115 mmol, 2.0 equiv.) and propargyl bromide (9.3 mL, 86 mmol 1.5 equiv.) to give the product as a pale yellow oil. (60 %); ν_{max}/cm^{-1} 3441 (O-H), 3310 (≡C-H), 2923 (C-H), 2853 (C-H), 2102 ($-N_3$), 1738 (O=C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.4 Hz, 2H, $HC{\equiv}CCH_2O$), 3.76 – 3.46 (m, 1H, $CH_2CH(OH)$), 3.26 – 3.14 (m, 1H, $(N_3)CHCH_2$), 2.49 (t, *J* = 2.4 Hz, 1H, $HC{\equiv}CCH_2O$), 2.35 (t, *J* = 7.5 Hz, 2H, $O{=}CCH_2$), 1.71 – 1.58 (m, 4H, $O{=}CCH_2CH_2$, $(N_3)CHCH_2$), 1.53 – 1.22 (m, 22H, $CH_2CH(OH)$, $CH(N_3)CH_2CH(OH)$, $(N_3)CHCH_2CH_3$, CH_2), 0.88 (t, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.93 ($O{=}CCH_2$, 77.74 ($HC{\equiv}CCH_2O$), 74.77

(HC≡*C*CH$_2$O), 73.52 (CH$_2$*C*H(OH)), 73.46 (CH$_2$*C*H(OH)), 67.10 ((N$_3$)*C*HCH$_2$), 67.04 ((N$_3$)*C*HCH$_2$), 51.74 (HC≡C*C*H$_2$O), 34.19 (O=C*C*H$_2$), 34.13 (O=C*C*H$_2$), 33.93 (O=C*C*H$_2$), 33.88 (O=C*C*H$_2$), 31.88 (*C*H$_2$CH(OH)), 31.82 (*C*H$_2$CH(OH)), 31.80 (*C*H$_2$CH(OH)), 30.78 (O=CCH$_2$*C*H$_2$), 30.74 (O=CCH$_2$*C*H$_2$), 29.64 (*C*H$_2$), 29.56 (*C*H$_2$), 29.49 (*C*H$_2$), 29.43 (*C*H$_2$), 29.41 (*C*H$_2$), 29.29 (*C*H$_2$), 29.22 (*C*H$_2$), 29.18 (*C*H$_2$), 29.11 (*C*H$_2$), 29.06 (*C*H$_2$), 29.00 (*C*H$_2$), 28.88 (*C*H$_2$), 28.86 (*C*H$_2$), 26.23 (*C*H$_2$), 26.15 (*C*H$_2$), 25.62 (*C*H$_2$), 25.51 (*C*H$_2$), 24.69 ((N$_3$)CH*C*H$_2$), 22.61 (*C*H$_2$), 14.06 (*C*H$_3$), 13.94 (*C*H$_3$); *m/z* (ES$^+$) [M+Na$^+$] 459.3 (C18:2), [M+Na$^+$] 402.3 (C18:1).

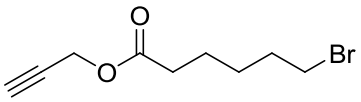
Prop-2-ynyl 10,13-diazido-9,12-dihydroxyoctadecanoate (SBE 4.7) (Synthesised from soybean oil)



The general procedure for the synthesis of azido propargyl fatty esters was applied using **SBO 4.12** (21.4 g, 53 mmol, 1.0 equiv.), K_2CO_3 (14.6 g, 105 mmol, 2.0 equiv.) and propargyl bromide (8.7 mL, 79 mmol, 1.5 equiv.) to give the product as a pale yellow oil. (59 %); ν_{max}/cm^{-1} 3415 (O-H), 3310 (≡C-H) 2923 (C-H), 2854 (C-H), 2101 (N=N$^+$=N$^-$), 1738 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.5 Hz, 2H, HC≡CC*H*$_2$O), 3.93 – 3.46 (m, 1.5H, CH$_2$C*H*(OH)), 3.32 – 2.95 (m, 1.5H, (N$_3$)C*H*CH$_2$), 2.50 (t, *J* = 2.6 Hz, 1H, *H*C≡CCH$_2$O), 2.35 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2$), 1.71 – 1.59 (m, 4H, O=CCH$_2$C*H*$_2$, (N$_3$)CHC*H*$_2$), 1.54 – 1.23 (m, 21H, C*H*$_2$CH(OH), C*H*$_2$, CH(N$_3$)C*H*$_2$CH(OH), (N$_3$)CHCH$_2$C*H*$_3$), 0.90 (t, *J* = 7.1 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.90 (O=*C*CH$_2$), 172.83 (O=*C*CH$_2$), 77.60 (H*C*≡CCH$_2$O), 74.68 (HC≡*C*CH$_2$O), 74.63 (HC≡*C*CH$_2$O), 73.57 (CH$_2$*C*H(OH)),

73.40 ($CH_2CH(OH)$), 73.35 ($CH_2CH(OH)$), 73.02 ($CH_2CH(OH)$), 72.92 ($CH_2CH(OH)$), 70.35 ($CH_2CH(OH)$), 70.13 ($CH_2CH(OH)$), 67.51 ($(N_3)CHCH_2$), 67.46 ($(N_3)CHCH_2$), 67.30 ($(N_3)CHCH_2$), 67.24 ($(N_3)CHCH_2$), 66.94 ($(N_3)CHCH_2$), 66.87 ($(N_3)CHCH_2$), 66.74 ($(N_3)CHCH_2$), 66.65 ($(N_3)CHCH_2$), 66.60 ($(N_3)CHCH_2$), 66.54 ($(N_3)CHCH_2$), 64.08 ($CH_2CH(OH)$), 63.98 ($CH_2CH(OH)$), 63.57 ($CH_2CH(OH)$), 63.45 ($CH_2CH(OH)$), 51.62 ($HC{\equiv}CCH_2O$), 51.59 ($HC{\equiv}CCH_2O$), 34.15 ($O{=}CCH_2$), 34.10 ($O{=}CCH_2$), 34.03 ($O{=}CCH_2$), 33.97 ($O{=}CCH_2$), 33.89 ($O{=}CCH_2$), 33.80 ($O{=}CCH_2$), 33.73 ($O{=}CCH_2$), 31.74 (CH_2), 31.68 (CH_2), 31.66 (CH_2), 31.57 (CH_2), 31.44 (CH_2), 30.64 ($O{=}CCH_2CH_2$), 30.60 ($O{=}CCH_2CH_2$), 30.56 ($O{=}CCH_2CH_2$), 30.53 ($O{=}CCH_2CH_2$), 30.31 ($O{=}CCH_2CH_2$), 30.28 ($O{=}CCH_2CH_2$), 29.95 (CH_2), 29.50 (CH_2), 29.40 (CH_2), 29.35 (CH_2), 29.28 (CH_2), 29.25 (CH_2), 29.17 (CH_2), 29.08 (CH_2), 29.04 (CH_2), 28.92 (CH_2), 28.87 (CH_2), 28.83 (CH_2), 28.72 (CH_2), 28.69 (CH_2), 26.10 (CH_2), 26.01 (CH_2), 25.93 (CH_2), 25.88 (CH_2), 25.72 (CH_2), 25.68 (CH_2), 25.48 (CH_2), 25.38 (CH_2), 25.28 (CH_2), 25.25 (CH_2), 25.15 (CH_2), 24.63 ($(N_3)CHCH_2$), 24.53 ($(N_3)CHCH_2$), 22.50 (CH_2), 22.47 (CH_2), 22.40 (CH_2), 22.34 (CH_2), 13.93 (CH_3), 13.80 (CH_3); *m/z* (ES^+) [$M+Na^+$] 459.3 (C18:2), [$M+Na^+$] 402.3 (C18:1).

6.4.5 Synthesis of prop-2-ynyl 6-bromohexanoate (4.15)



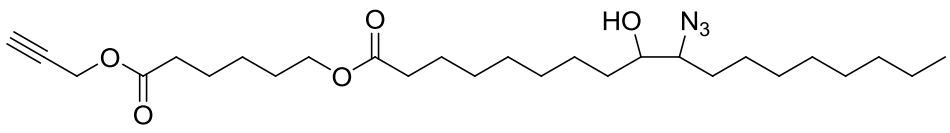
6-Bromohexanoic acid **4.14** (60.0 g, 0.31 mol, 1.0 equiv.) was dissolved in acetonitrile (500 mL, 0.6 M) at 60 °C. K_2CO_3 (85.0 g, 0.62 mol, 2.0 equiv.) was added and left for 10 mins when propargyl bromide (80 wt. % in toluene) (66.3 mL, 0.62 mol, 2.0 equiv.) was added and reacted overnight at 50 °C. The reaction mixture was diluted with chloroform and water. The organic layer was washed with

saturated NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* and purification achieved through silica plug (4:1 pet ether:ethyl acetate) to give pure product (76 %) ν_{max}/cm^{-1} 3300 (≡C-H), 2975 (C-H), 2910 (C-H), 1730 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.5 Hz, 2H, HC≡CC*H*$_2$O), 3.41 (t, *J* = 6.7 Hz, 2H, CH_2CH_2Br), 2.53 (t, *J* = 2.5 Hz, 1H, *H*C≡CCH_2O), 2.38 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2$$CH_2CH_2$), 1.88 (tt, *J* = 6.9 Hz, 2H, C*H*$_2$$CH_2Br$), 1.68 (tt, *J* = 7.4 Hz, 2H, $O=CCH_2CH_2CH_2$), 1.49 (tt, *J* = 8.2, 7.1 Hz, 2H, $O=CCH_2CH_2CH_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.46 (O=*C*CH_2CH_2), 77.72 (H*C*≡CCH_2O), 74.91 (HC≡*C*CH_2O), 51.80 (HC≡C*C*H_2O), 33.64 (O=C*C*$H_2CH_2CH_2$, 33.46 (CH_2*C*H_2Br), 32.29 (*C*H_2CH_2Br), 27.49 ($O=CCH_2CH_2$*C*H_2), 23.87 ($O=CCH_2$*C*H_2CH_2); *m/z* (ES^+) 255.0 $[M+Na]^+$

6.4.6 General Procedure for the synthesis of extended azido propargyl fatty esters

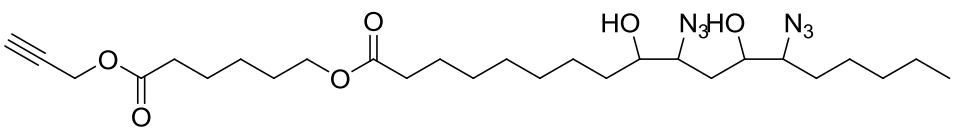
The desired azido fatty acid (1 equiv.) was dissolved in DMF (0.25 M) at 50 °C, K_2CO_3 (2 equiv.) and prop-2-ynyl 6-bromohexanoate (1 equiv.) were added and reacted overnight at 50 °C. The reaction mixture was diluted with water (200 mL) and extracted with chloroform. The organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* and purification was achieved through silica plug (4:1 pet ether:ethyl acetate) to give pure product.

6-Oxo-6-(prop-2-ynyloxy)hexyl 10-azido-9-hydroxyoctadecanoate (ExOE 4.8)



The general procedure for the synthesis of extended azido propargyl fatty esters was applied using **oleic 4.12** (25.0 g, 73 mmol, 1.0 equiv.), K_2CO_3 (20.2 g, 146 mmol, 2.0 equiv.) and **4.15** (17.1 g, 73 mmol, 1.0 equiv.) to give the product as a pale yellow oil. (51 %); ν_{max}/cm^{-1} 3487 (O-H), 3299 (≡C-H), 2925 (C-H), 2855 (C-H), 2100 (-N_3), 1733 (O=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 4.06 (t, *J* = 6.6 Hz, 2H, CH_2CH_2O), 3.54 (dt, *J* = 11.5, 5.4 Hz, 1H, CH_2CH(OH)), 3.18 (dt, *J* = 11.1, 6.7 Hz, 1H, (N_3)C*H*CH_2), 2.51 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH_2O), 2.37 (t, *J* = 7.5 Hz, 2H, HC≡CC*H*$_2$OO=CC*H*$_2$$CH_2$), 2.29 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$$CH_2$), 1.73 – 1.56 (m, 8H, $CH_2CH_2CH_2O$, (N_3)CHC*H*$_2$, HC≡CCH_2OO=CCH_2C*H*$_2$, O=CCH_2C*H*$_2$), 1.55 – 1.19 (m, 24H, C*H*$_2$$CH_2CH_2O$, C*H*$_2$CH(OH), C*H*$_2$), 0.88 (t, *J* = 6.5 Hz, 3H, CH_2C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64 (O=*C*CH_2CH_2), 172.40 (HC≡CCH_2OO=*C*CH_2CH_2), 77.53 (H*C*≡CCH_2O), 74.69 (HC≡*C*CH_2O), 73.33 (CH_2*C*H(OH)), 73.27 (CH_2*C*H(OH)), 66.86 ((N_3)*C*HCH_2), 66.81 ((N_3)*C*HCH_2), 63.80 (CH_2*C*H_2O), 51.61 (HC≡C*C*H_2O), 34.05 (O=C*C*$H_2$$CH_2$), 33.94 (*C*$H_2$CH(OH)) 33.56 (HC≡C$CH_2$OO=C*C*$H_2$$CH_2$), 31.65 (C*H*$_2$), 30.55 (C*H*$_2$), 29.40 (C*H*$_2$), 29.32 (C*H*$_2$), 29.27 (C*H*$_2$), 29.17 (C*H*$_2$), 29.06 (C*H*$_2$), 29.01 (C*H*$_2$), 28.95 (C*H*$_2$), 28.89 (C*H*$_2$), 28.82 (C*H*$_2$), 28.09 (C*H*$_2$), 27.34 (C*H*$_2$), 26.09 (C*H*$_2$), 26.02 (C*H*$_2$), 25.46 (C*H*$_2$), 25.38 (C*H*$_2$), 25.24 (C*H*$_2$), 24.70 (C*H*$_2$), 24.20 (C*H*$_2$), 22.44 (C*H*$_2$), 13.90 (*C*$H_3$).; *m/z* ($ES^+$) [M+$Na^+$] 516.3 (C18:1);

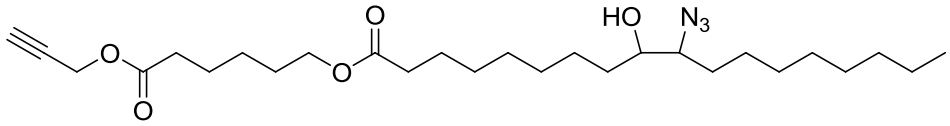
6-Oxo-6-(prop-2-ynyloxy)hexyl-10,13-diazido-9,12-dihydroxyoctadecanoate (ExLE 4.8)



The general procedure for the synthesis of extended azido propargyl fatty esters was applied using **linoleic 4.12** (20 g, 50 mmol, 1.0 equiv.), K_2CO_3 (13.8 g, 100 mmol, 2.0 equiv.) and **4.15** (11.7 g, 50 mmol, 1.0 equiv.) to give the product as a pale yellow oil. (60 %); ν_{max}/cm^{-1} 3494 (O-H), 3306 (≡C-H), 2928 (C-H), 2856 (C-H), 2102 (-N_3), 1730 (O=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 4.06 (t, *J* = 6.6 Hz, 2H, CH_2CH_2O), 3.94 – 3.47 (m, 1.5H, CH_2CH(OH)), 3.47 – 3.09 (m, 1.5H, (N_3)C*H*CH_2), 2.49 (t, *J* = 2.3 Hz, 1H, *H*C≡CCH_2O), 2.38 (t, *J* = 7.4 Hz, 2H, HC≡CC*H*$_2$OO=CC*H*$_2CH_2$), 2.30 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2CH_2$), 1.78 – 1.56 (m, 8H, $CH_2CH_2CH_2O$, (N_3)CHC*H*$_2$, HC≡CCH_2OO=CCH_2CH_2, O=CCH_2CH_2)), 1.56 – 1.16 (m, 21H, C*H*$_2CH_2CH_2O$, C*H*$_2$CH(OH), C*H*$_2$), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.04 (O=*C*CH_2CH_2), 172.78 (HC≡CCH_2OO=*C*CH_2CH_2), 77.77 (H*C*≡CCH_2O), 74.92 (HC≡*C*CH_2O), 73.87 (CH_2*C*H(OH)), 73.63 (CH_2*C*H(OH)), 73.57 (CH_2*C*H(OH)), 73.26 (CH_2*C*H(OH)), 73.11 (CH_2*C*H(OH)), 70.53 (CH_2*C*H(OH)), 70.40 (CH_2*C*H(OH)), 70.37 (CH_2*C*H(OH)), 67.85 ((N_3)*C*$CHCH_2$), 67.54 ((N_3)*C*$CHCH_2$), 67.47 ((N_3)*C*$CHCH_2$), 67.25 ((N_3)*C*$CHCH_2$), 67.19 ((N_3)*C*$CHCH_2$), 66.99 ((N_3)*C*$CHCH_2$), 64.11 (CH_2*C*H_2O), 63.87 ((N_3)*C*$CHCH_2$), 63.75 ((N_3)*C*$CHCH_2$), 51.93 (HC≡C*C*H_2O), 34.34 (O=C*C*H_2CH_2), 33.87 (HC≡CCH_2OO=C*C*H_2CH_2), 31.92 (*C*H_2), 31.77 (*C*H_2), 31.67 (*C*H_2), 30.92 (*C*H_2), 30.82 (*C*H_2), 29.53 (*C*H_2), 29.42 (*C*H_2), 29.32 (*C*H_2), 29.26 (*C*H_2), 29.10 (*C*H_2), 29.02 (*C*H_2), 28.36 (*C*H_2), 26.33 (*C*H_2), 26.26 (*C*H_2), 25.92 (*C*H_2), 25.63 (*C*H_2), 25.52 (*C*H_2), 24.94 (*C*H_2), 24.48 (*C*H_2), 22.73 (*C*H_2), 22.63 (*C*H_2), 22.57 (*C*H_2), 14.26 (*C*H_3), 14.06 (*C*H_3).; *m/z* (ES^+) [$M+Na^+$] 573.3 (C18:2), [$M+Na^+$] 516.3 (C18:1).

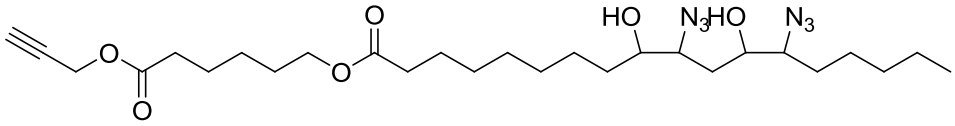
6-Oxo-6-(prop-2-ynyloxy)hexyl 10-azido-9-hydroxyoctadecanoate (RSE 4.8)

(Synthesised from rapeseed oil)



The general procedure for the synthesis of extended azido propargyl fatty esters was applied using **RSO 4.12** (23 g, 58 mmol, 1.0equiv.), K_2CO_3 (15.9 g, 115 mmol, 2.0equiv.) and **4.15** (13.4 g, 57 mmol, 1.0 equiv.) to give the product as a pale yellow oil. (61 %); ν_{max}/cm^{-1} 3459 (O-H), 3300 (≡C-H), 2927 (C-H), 2856 (C-H), 2100 (-N_3), 1732 (O=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.5 Hz, 2H, HC≡CC*H*$_2$O), 4.06 (t, *J* = 6.6 Hz, 2H, CH_2CH_2O), 3.57 – 3.48 (m, 1H, CH_2CH(OH)), 3.19 (dt, *J* = 11.1, 6.7 Hz, 1H, (N_3)C*H*CH_2), 2.49 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH_2O), 2.37 (t, *J* = 7.5 Hz, 2H, HC≡CC*H*$_2$OO=CC*H*$_2$$CH_2$), 2.29 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$$CH_2$), 1.73 – 1.56 (m, 8H, $CH_2CH_2CH_2O$, (N_3)CHC*H*$_2$, HC≡CCH_2OO=CCH_2C*H*$_2$, O=CCH_2C*H*$_2$), 1.56 – 1.18 (m, 24H, C*H*$_2$$CH_2CH_2O$, C*H*$_2$CH(OH), C*H*$_2$), 0.88 (t, *J* = 6.5 Hz, 3H, CH_2C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.81 (O=*C*CH_2CH_2), 172.59 (HC≡CCH_2OO=*C*CH_2CH_2), 77.66 (H*C*≡CCH_2O), 74.78 (HC≡*C*CH_2O), 73.44 (CH_2*C*H(OH)), 67.05 ((N_3)*C*HCH_2), 63.95 (CH_2*C*H_2O), 51.77 (HC≡C*C*H_2O), 34.22 (O=C*C*H_2CH_2), 33.74 (HC≡CCH_2OO=C*C*H_2CH_2), 31.79 (*C*H_2), 30.78 (*C*H_2), 29.53 (*C*H_2), 29.46 (*C*H_2), 29.41 (*C*H_2), 29.39 (*C*H_2), 29.30 (*C*H_2), 29.21 (*C*H_2), 29.19 (*C*H_2), 29.15 (*C*H_2), 29.09 (*C*H_2), 29.04 (*C*H_2), 28.97 (*C*H_2), 28.24 (*C*H_2), 26.21 (*C*H_2), 26.15 (*C*H_2), 25.59 (*C*H_2), 25.51 (*C*H_2), 25.40 (*C*H_2), 24.85 (*C*H_2), 24.36 (*C*H_2), 22.59 (*C*H_2), 14.05 (*C*H_3).; *m/z* (ES^+) [M+Na^+] 573.3 (C18:2), [M+Na^+] 516.3 (C18:1).

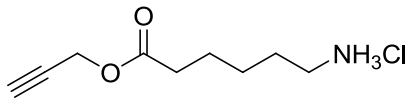
6-Oxo-6-(prop-2-ynyloxy)hexyl-10,13-diazido-9,12-dihydroxyoctadecanoate (SBE 4.8) (Synthesised from soybean oil)



The general procedure for the synthesis of extended azido propargyl fatty esters was was applied using **SBO 4.12** (18.8 g, 47 mmol, 1.0 equiv.), K_2CO_3 (13.1 g, 95 mmol, 2.0 equiv.) and **4.15** (11.0 g, 47 mmol, 1.0 equiv) to give the product as a pale yellow oil. (51 %); ν_{max}/cm^{-1} 3457 (O-H), 3299 (≡C-H), 2927 (C-H), 2856 (C-H), 2100 (-N_3), 1731 (O=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 4.06 (t, *J* = 6.6 Hz, 2H, CH_2CH_2O), 3.94 – 3.35 (m, 1.5H, CH_2CH(OH)), 3.28 – 3.11 (m, 1.5H, (N_3)C*H*CH_2), 2.49 (t, *J* = 2.3 Hz, 1H, *H*C≡CCH_2O), 2.38 (t, *J* = 7.4 Hz, 2H, HC≡CC*H*$_2$OO=CC*H*$_2CH_2$), 2.30 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2CH_2$), 1.73 – 1.54 (m, 8H, $CH_2CH_2CH_2O$, (N_3)CHC*H*$_2$, HC≡CCH_2OO=CCH_2CH_2, O=CCH_2CH_2), 1.53 – 1.16 (m, 23H, C*H*$_2CH_2CH_2O$, C*H*$_2$CH(OH), (N_3)$CHCH_2CH_3$ C*H*$_2$), 0.90 (t, *J* = 6.9 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.04 (O=*C*CH_2CH_2), 172.77 (HC≡CCH_2OO=*C*CH_2CH_2), 77.77 (H*C*≡CCH_2O), 74.92 (HC≡*C*CH_2O), 74.56 (CH_2CH(OH)), 74.47 (CH_2CH(OH)), 73.87 (CH_2CH(OH)), 73.63 (CH_2CH(OH)), 73.57 (CH_2CH(OH)), 73.26 (CH_2CH(OH)), 73.12 (CH_2CH(OH)), 70.52 (CH_2CH(OH)), 70.40 (CH_2CH(OH)), 70.36 (CH_2CH(OH)), 67.80 ((N_3)*C*HCH_2), 67.54 ((N_3)*C*HCH_2), 67.47 ((N_3)*C*HCH_2), 67.25 ((N_3)*C*HCH_2), 67.18 ((N_3)*C*HCH_2), 66.98((N_3)*C*HCH_2), 66.91((N_3)*C*HCH_2), 64.12 (CH_2CH_2O), 63.88 (CH_2CH(OH)), 63.74 (CH_2CH(OH)), 51.93 (HC≡C*C*H_2O), 34.34 (O=C*C*H_2CH_2), 33.87 (HC≡CCH_2OO=C*C*H_2CH_2), 31.91 (CH_2), 31.67 (CH_2), 30.81 (CH_2), 30.56 (CH_2), 29.52 (CH_2), 29.26 (CH_2), 29.09 (CH_2), 28.35 (CH_2),

26.26 (CH_2), 25.94 (CH_2), 25.62 (CH_2), 25.52 (CH_2), 24.93 (CH_2), 24.48 (CH_2), 22.73 (CH_2), 22.57 (CH_2), 14.18 (CH_3), 14.06 (CH_3).; *m/z* (ES^+) [$M+Na^+$] 573.3 (C18:2), [$M+Na^+$] 516.3 (C18:1).

6.4.6 Synthesis of prop-2-ynyl 6-aminohexanoate (4.18)



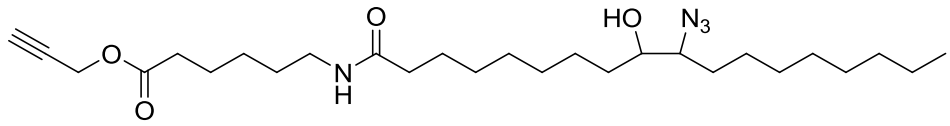
6-aminohexanoic acid **4.17** (20.0 g, 152 mmol, 1.0 equiv.) was dissolved in propargyl alcohol (170 mL, 0.6 M) at room temperature. Thionyl chloride (13.3 mL, 183 mmol, 1.2 equiv.) was added dropwise and left for 1 hour. The reaction was concentrated *in vacuo* then triturated using hexane to give pure product as a hydrochloride salt. ν_{max}/cm^{-1} 3254 (H-N, ≡C-H), 2955 (C-H), 2910 (C-H), 1730 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 3H, N*H*$_3$Cl), 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 3.02 (s, 2H, $CH_2CH_2NH_3Cl$), 2.51 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH_2O), 2.39 (t, *J* = 7.3 Hz, 2H, O=CC*H*$_2$$CH_2$), 1.82 (tt, *J* = 7.7, 7.2 Hz, 2H, C*H*$_2$$CH_2NH_3Cl$), 1.69 (tt, *J* = 7.4 Hz, 2H, O=CCH_2C*H*$_2$), 1.46 (tt, *J* = 7.7, 7.0 Hz, 2H, O=CCH_2CH_2C*H*$_2$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.74 (O=*C*CH_2CH_2), 77.83 (H*C*≡CCH_2O), 75.11 (HC≡*C*CH_2O), 52.08 (HC≡C*C*H$_2$O), 39.88 (CH_2*C*H_2NH_3Cl), 33.69 (O=C*C*H_2CH_2), 27.28 (*C*$H_2CH_2NH_3Cl$), 25.96 (O=CCH_2CH_2*C*H$_2$), 24.19 (O=CCH_2*C*H_2CH_2).; *m/z* (ES^+) 170.1 $[M+H]^+$.

6.4.7 General Procedure for the synthesis of prop-2-ynyl 6-aminohexanoate fatty amides

The desired azido fatty acid (1.0 equiv.) and NMM (1.2 equiv.) were dissolved in THF (0.7 M) at 0 °C, ethyl chloroformate (1.2 equiv.) was added and left to react for 1 h. NMM.HCl was filtered off and the filtrate added dropwise to a solution of prop-

2-ynyl 6-aminohexanoate (1.0 equiv) and TEA (2.0 equiv) dissolved in DMF (25 mL) and left to react overnight. The reaction mixture was diluted with Et_2O and washed with aqueous acid (100 ml 2 M HCl), sodium hydrogen carbonate (100 mL 2 M) and saturated NaCl (100 mL). The organic layer was dried over $MgSO_4$ solvent removed *in vacuo* to give crude product which was purified through silica plug (1:1 pet ether:ethyl acetate) to give pure product

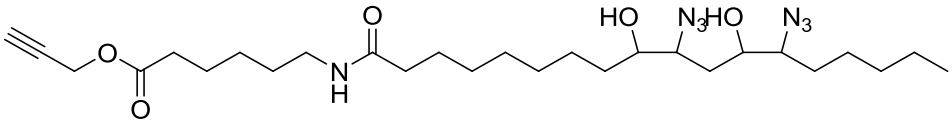
Prop-2-ynyl 6-(10-azido-9-hydroxyoctadecanamido)hexanoate (ExOA 4.9)



The general procedure for the synthesis of prop-2-ynyl 6-aminohexanoate fatty amides was applied using **oleic 4.12** (1.5 g, 4.0 mmol, 1.0 equiv.), NMM (0.5 mL, 4.7 mmol, 1.1 equiv.) and ethyl chloroformate (0.5 mL, 4.7 mmol, 1.1 equiv.) followed by **4.18** (1.0 g, 4.7 mmol, 1.1 equiv) and TEA (1.3 mL, 9.4 mmol, 2.2 equiv) to give the product as a yellow oil. (71 %); ν_{max}/cm^{-1} 3310 (H-N, ≡C-H), 2926 (C-H), 2855 (C-H), 2101 ($N=N^+=N^-$) 1740 (OC=O) 1649 (HNC=O); ^1H NMR (300 MHz, $CDCl_3$) δ 5.50 (s, 1H, N*H*), 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CCH_2O), 3.69 – 3.51 (m, 1H, CH_2CH(OH), 3.32 – 3.08 (m, 3H, $(N_3)CHCH_2$, CH_2CH_2NH), 2.48 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH_2O), 2.36 (t, *J* = 7.4 Hz, 2H, HNO=CCH_2CH_2), 2.15 (t, *J* = 7.5 Hz, 2H, O=CCH_2CH_2), 1.76 – 1.56 (m, 6H, HNO=CCH_2CH_2, O=CCH_2CH_2, $(N_3)CHCH_2$), 1.55 – 1.45 (m, 4H, $CH_2CH_2CH_2$NH, $CH_2CH_2CH_2$NH), 1.39 – 1.23 (m, 22H, CH_2CH(OH), CH_2), 0.88 (t, *J* = 6.0 Hz, 3H, CH_3).; ^{13}C NMR (75 MHz, CDCl3) δ 173.20 (O=*C*CH_2CH_2), 172.87 (HNO=*C*CH_2CH_2), 77.36 (H*C*≡CCH_2O), 74.94 (HC≡*C*CH_2O), 73.67 (CH_2CH(OH)), 73.62 (CH_2CH(OH)), 67.37 ($(N_3)CHCH_2$), 67.26 ($(N_3)CHCH_2$), 51.97 (HC≡CCH_2O), 39.28 (CH_2CH_2NH), 36.94

(O=C*C*H_2CH_2), 33.88 (HNO=C*C*H_2CH_2), 31.98 (*C*H_2), 31.01 (*C*H_2), 29.64 (*C*H_2), 29.41 (*C*H_2), 29.26 (*C*H_2), 26.38 (*C*H_2), 25.81 (*C*H_2), 24.45 (*C*H_2), 22.79 (*C*H_2), 14.24 (*C*H_3).; *m/z* (ES^+) 515.3 $[M+Na]^+$ (C18:1).

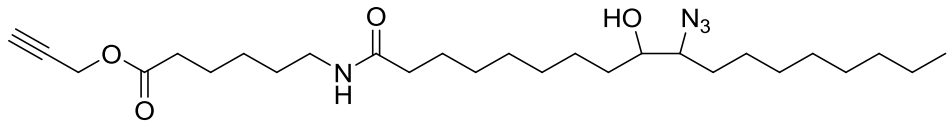
Prop-2-ynyl 6-(10,13-diazido-9,12-dihydroxyoctadecanamido)hexanoate (ExLA 4.9)



The general procedure for the synthesis of prop-2-ynyl 6-aminohexanoate fatty amides was applied using **linoleic 4.12** (1.9 g, 4.8 mmol, 1.0 equiv.), NMM (0.6 mL, 5.3 mmol, 1.1 equiv.) and ethyl chloroformate (0.5 mL, 5.3 mmol, 1.1 equiv.) followed by **4.18** (1.1 g, 5.3 mmol, 1.1 equiv) and TEA (1.5 mL, 10 mmol, 2.2 equiv) to give the product as a pale yellow oil. (90 %); ν_{max}/cm^{-1} 3306 (H-N, ≡C-H), 2926 (C-H), 2855 (C-H), 2101 ($N=N^+=N^-$) 1739 (OC=O) 1645 (HNC=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (s, 1H, N*H*), 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 3.98 – 3.53 (m, 1.5H, CH_2C*H*(OH)), 3.30 – 3.18 (m, 3.5H, (N_3)C*H*CH_2, CH_2C*H*$_2$NH), 2.49 (t, *J* = 2.5 Hz, 1H, *H*C≡CCH_2O), 2.37 (t, *J* = 7.4 Hz, 2H, HNO=CC*H*$_2$CH_2), 2.16 (t, *J* = 7.3 Hz, 2H, O=CC*H*$_2$CH_2), 1.72 – 1.56 (m, 7H, HNO=CCH_2C*H*$_2$, O=CCH_2C*H*$_2$, (N_3)CHC*H*$_2$), 1.54 – 1.46 (m, 4H, C*H*$_2$CH_2CH_2NH, CH_2C*H*$_2$CH_2NH), 1.44 – 1.24 (m, 20H, C*H*$_2$CH(OH), C*H*$_2$), 0.89 (t, *J* = 7.0 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.47 (O=*C*CH_2CH_2), 172.91 (HNO=*C*CH_2CH_2), 77.80 (H*C*≡CCH_2O), 74.95 (HC≡*C*CH_2O), 74.54 (CH_2*C*H(OH)), 73.87 (CH_2*C*H(OH)), 73.64 (CH_2*C*H(OH)), 73.59 (CH_2*C*H(OH)), 73.18 (CH_2*C*H(OH)), 70.40 (CH_2*C*H(OH)), 70.07 (CH_2*C*H(OH)), 67.49 ((N_3)*C*HCH_2), 67.27 ((N_3)*C*HCH_2), 67.19 ((N_3)*C*HCH_2), 66.90 ((N_3)*C*HCH_2), 63.76 ((N_3)*C*HCH_2), 51.95 (HC≡C*C*H_2O), 39.28 (CH_2*C*H_2NH),

36.81 (O=C*C*H_2CH_2), 33.84 (HNO=C*C*H_2CH_2), 31.94 (*C*H_2), 31.70 (*C*H_2), 30.81 (*C*H_2), 30.61 (*C*H_2), 29.79 (*C*H_2), 29.68 (*C*H_2), 29.61 (*C*H_2), 29.31 (*C*H_2), 29.22 (*C*H_2), 29.06 (*C*H_2), 28.95 (*C*H_2), 26.33 (*C*H_2), 25.97 (*C*H_2), 25.78 (*C*H_2), 25.63 (*C*H_2), 24.82 (*C*H_2), 24.40 (*C*H_2), 22.75 (*C*H_2), 22.66 (*C*H_2), 22.60 (*C*H_2), 14.20 (*C*H_3), 14.09 (*C*H_3).; *m/z* (ES^+) 572.2 $[M+Na]^+$ (C18:2), 515.3 $[M+Na]^+$ (C18:1).

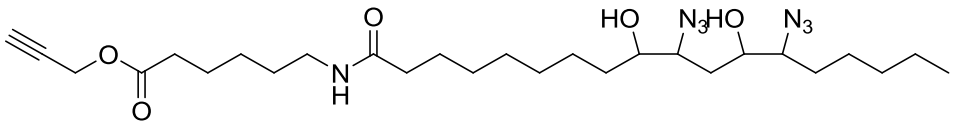
Prop-2-ynyl 6-(10-azido-9-hydroxyoctadecanamido)hexanoate (ExRSA 4.9) (Synthesised from rapeseed oil)



The general procedure for the synthesis of prop-2-ynyl 6-aminohexanoate fatty amides was applied using **RSO 4.12** (5.8 g, 14 mmol, 1.0 equiv.), NMM (1.8 mL, 16 mmol, 1.1 equiv.) and ethyl chloroformate (1.8 mL, 16 mmol, 1.1 equiv.) followed by **4.18** (3.3 g, 16 mmol, 1.1 equiv) and TEA (4.5 mL, 32 mmol, 2.2 equiv) to give the product as a pale yellow oil. (56 %); ν_{max}/cm^{-1} 3307 (H-N, ≡C-H), 2924 (C-H), 2854 (C-H), 2099 (N=N^+=N^-) 1739 (OC=O) 1643 (HNC=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (s, 1H, N*H*), 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 3.73 – 3.42 (m, 1H, CH_2C*H*(OH)), 3.31 – 3.13 (m, 3H, (N_3)C*H*CH_2, CH_2C*H*$_2$NH), 2.49 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH_2O), 2.37 (t, *J* = 7.4 Hz, 2H, HNO=CC*H*$_2$CH_2), 2.16 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$CH_2), 1.72 – 1.58 (m, 6H, HNO=CCH_2C*H*$_2$, O=CCH_2C*H*$_2$, (N_3)CHC*H*$_2$), 1.56 – 1.46 (m, 4H, C*H*$_2$CH_2CH_2NH, CH_2C*H*$_2$CH_2NH), 1.41 – 1.25 (m, 22H, C*H*$_2$CH(OH), C*H*$_2$), 0.88 (t, *J* = 6.4 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.31 (O=*C*CH_2CH_2), 172.86 (HNO=*C*CH_2CH_2), 77.79 (H*C*≡CCH_2O), 74.93 (HC≡*C*CH_2O), 73.62 (CH_2*C*H(OH)), 73.57 (CH_2*C*H(OH)), 67.29 ((N_3)*C*HCH_2), 67.17 ((N_3)*C*HCH_2), 51.93 (HC≡C*C*H_2O), 39.25 (CH_2*C*H_2NH), 36.87

(O=C*C*H_2CH_2), 33.83 (HNO=C*C*H_2CH_2), 31.92 (*C*H_2), 30.93 (*C*H_2), 30.88 (*C*H_2), 29.67 (*C*H_2), 29.60 (*C*H_2), 29.56 (*C*H_2), 29.41 (*C*H_2), 29.33 (*C*H_2), 29.21 (*C*H_2), 26.33 (*C*H_2), 25.78 (*C*H_2), 25.62 (*C*H_2), 24.40 (*C*H_2), 22.74 (*C*H_2), 14.20 (*C*H_3).; *m/z* (ES^+) 572.2 $[M+Na]^+$ (C18:2), 515.3 $[M+Na]^+$ (C18:1).

Prop-2-ynyl-6-(10,13-diazido-9,12-dihydroxyoctadecanamido)hexanoate (ExSBA 4.9) (Synthesised from soybean oil)



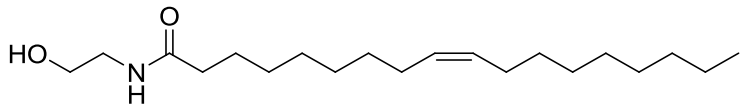
The general procedure for the synthesis of prop-2-ynyl 6-aminohexanoate fatty amides was applied **SBO 4.12** (5.8 g, 14 mmol, 1.0 equiv.), NMM (1.8 mL, 16 mmol, 1.1 equiv.) and ethyl chloroformate (1.8 mL, 16 mmol, 1.1 equiv.) followed by **4.18** (3.3 g, 16 mmol, 1.1 equiv) and TEA (4.5 mL, 32 mmol, 2.2 equiv) to give the product as a pale yellow oil. (53 %); ν_{max}/cm^{-1} 3308 (H-N, ≡C-H), 2926 (C-H), 2855 (C-H), 2101 (N=N^+=N^-) 1739 (OC=O) 1645 (HNC=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (s, 1H, N*H*), 4.68 (d, *J* = 2.4 Hz, 2H, HC≡CCH_2O), 3.98 – 3.52 (m, 1.5H, CH_2C*H*(OH)), 3.29 – 3.11 (m, 3.5H, (N_3)C*H*CH_2, CH_2CH_2NH), 2.49 (t, *J* = 2.3 Hz, 1H, *H*C≡CCH_2O), 2.37 (t, *J* = 7.4 Hz, 2H, HNO=CC$H_2$$CH_2$), 2.16 (t, *J* = 7.2 Hz, 2H, O=CC$H_2$$CH_2$), 1.71 – 1.58 (m, 7H, HNO=CCH_2CH_2, O=CCH_2CH_2, (N_3)CHCH_2), 1.56 – 1.46 (m, 4H, C$H_2$$CH_2$$CH_2NH, CH_2CH_2$$CH_2$NH), 1.42 – 1.25 (m, 20H, CH_2CH(OH), CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.43 (O=*C*$CH_2$$CH_2$), 172.92 (HNO=*C*$CH_2$$CH_2$), 77.80 (H*C*≡C$CH_2$O), 74.96 (HC≡*C*$CH_2$O), 73.87 ($CH_2$*C*H(OH)), 73.64 ($CH_2$*C*H(OH)), 73.19 ($CH_2$*C*H(OH)), 72.87 ($CH_2$*C*H(OH)), 70.41 ($CH_2$*C*H(OH)), 70.07 ($CH_2$*C*H(OH)), 67.50 (($N_3$)*C*H$CH_2$), 67.28 (($N_3$)*C*H$CH_2$), 67.19 (($N_3$)*C*H$CH_2$), 66.90 (($N_3$)*C*H$CH_2$),

63.86 ($(N_3)CHCH_2$), 63.77 ($(N_3)CHCH_2$), 51.96 ($HC{\equiv}CCH_2O$), 39.29 (CH_2CH_2NH), 36.82 ($O{=}CCH_2CH_2$), 33.84 ($HNO{=}CCH_2CH_2$), 31.95 (CH_2), 31.71 (CH_2), 30.61 (CH_2), 29.79 (CH_2), 29.61 (CH_2), 29.32 (CH_2), 29.22 (CH_2), 29.06 (CH_2), 28.95 (CH_2), 26.33 (CH_2), 25.98 (CH_2), 25.79 (CH_2), 25.63 (CH_2), 25.40 (CH_2), 24.40 (CH_2), 22.76 (CH_2), 22.61 (CH_2), 14.29 (CH_3), 14.09 (CH_3).; *m/z* (ES^+) 572.2 $[M+Na]^+$ (C18:2), 515.3 $[M+Na]^+$ (C18:1).

6.4.8 General Procedure for the synthesis of ethanolamine fatty amides

The desired fatty acid (1 equiv.) and ethanolamine (1 equiv.) were reacted overnight at 150 °C. The reaction mixture was quenched by pouring into ice cold water (200 mL) and extracted with ethyl acetate. The organic layer was washed with 15 % NaCL and dried over $MgSO_4$. The solvent was removed *in vacuo* to give pure product.

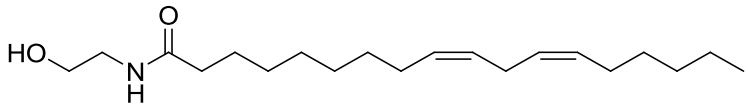
N-(2-hydroxyethyl)oleamide (OA 4.20)



The general procedure for the synthesis of ethanolamine fatty amides was applied using oleic acid **1.22** (25.0 g, 89 mmol, 1.0 equiv.) and ethanolamine (8.0 mL, 132 mmol, 1.5 equiv.) to give the product as a pale yellow oil. (84 %); ν_{max}/cm^{-1} 3293 (H-N, O-H), 2919 (C-H), 2849 (C-H), 1642 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 1H, N*H*), 5.40 – 5.27 (m, 2H, *H*C=C*H*), 4.22 (s (br), 1H, O*H*), 3.69 (t, *J* = 5.0 Hz, 2H, $HOCH_2CH_2NH$), 3.39 (dt, *J* = 5.2 Hz, 2H, $HOCH_2CH_2NH$), 2.20 (t, *J* = 7.6 Hz, 2H, $O{=}CCH_2CH_2$), 2.08 – 1.91 (m, 4H, $=CHCH_2$), 1.68 – 1.54 (m, 2H, $O{=}CCH_2CH_2$), 1.40 – 1.18 (m, 20H, CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.76 ($O{=}CCH_2CH_2$), 130.06 (H*C*=*C*H), 129.72 (H*C*=*C*H),

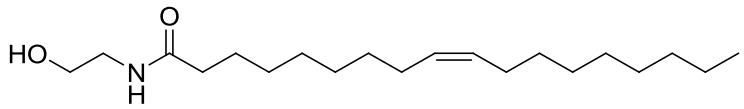
61.94 (HO*C*$H_2$$CH_2$NH), 42.39 (HOC$H_2$*C*$H_2$NH), 36.69 (O=C*C*$H_2$$CH_2$), 31.95 (*C*$H_2$), 29.81 (*C*$H_2$), 29.78 (*C*$H_2$), 29.58 (*C*$H_2$), 29.37 (*C*$H_2$), 29.23 (*C*$H_2$), 27.27 (=CH*C*$H_2$), 27.23 (=CH*C*$H_2$), 25.84 (O=CC$H_2$*C*$H_2$), 22.73 (*C*$H_2$), 14.17 (*C*$H_3$).;*m/z* ($ES^+$) 348.1 $[M+Na]^+$ (C18:1).

N-(2-hydroxyethyl)linoleamide (LA 4.20)



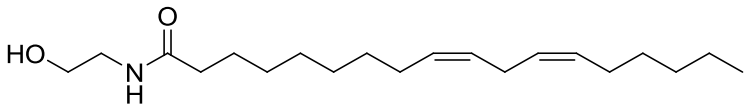
The general procedure for the synthesis of ethanolamine fatty amides was applied using linoleic acid **1.23** (25.0 g, 89 mmol, 1.0 equiv.) and ethanolamine (8.0 mL, 132 mmol, 1.5 equiv.) to give the product as a pale yellow waxy solid. (84 %); νmax/cm^{-1} 3300 (H-N, O-H), 2922 (C-H), 2842 (C-H), 1641 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H, N*H*), 5.48 – 5.26 (m, 3H, *H*C=C*H*), 4.30 (br s, 1H, O*H*), 3.67 (t, J = 5.1 Hz, 2H, HOC*H*$_2$$CH_2$NH), 3.37 (dt, J = 5.2 Hz, 2H, HOCH_2C*H*$_2$NH), 2.84 – 2.69 (m, 1H, HC=CHC*H*$_2$CH=CH), 2.20 (t, J = 7.5 Hz, 2H, O=CC*H*$_2$$CH_2$), 2.11 – 1.91 (m, 3H, =CHC*H*$_2$$CH_2$), 1.68 – 1.52 (m, 2H, O=CCH_2C*H*$_2$), 1.46 – 1.04 (m, 15H, C*H*$_2$), 0.97 (t, J = 7.5 Hz, 0.2H, =CHCH_2C*H*$_3$) 0.92 – 0.85 (m, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.80 (O=*C*C$H_2$$CH_2$), 130.21 (H*C*=*C*H), 130.00 (H*C*=*C*H), 129.96 (H*C*=*C*H), 129.67 (H*C*=*C*H), 128.06 (H*C*=*C*H), 127.87 (H*C*=*C*H), 61.64 (HO*C*$H_2$$CH_2$NH), 42.25 (HOC$H_2$*C*$H_2$NH), 36.61 (O=C*C*$H_2$$CH_2$), 31.90 (*C*$H_2$), 31.51 (*C*$H_2$), 29.75 (*C*$H_2$), 29.64 (*C*$H_2$), 29.53 (*C*$H_2$), 29.33 (*C*$H_2$), 29.32 (*C*$H_2$), 29.19 (*C*$H_2$), 27.19 (=CH*C*$H_2$), 25.80 (O=CC$H_2$*C*$H_2$), 25.61 (HC=CH*C*$H_2$CH=CH), 22.68 (*C*$H_2$), 22.57 (*C*$H_2$), 14.28 (=CHC$H_2$*C*$H_3$), 14.12 (*C*$H_3$), 14.08 (*C*$H_3$).; m/z (ES+) 348.1 $[M+Na]^+$ (C18:1), 346.1 $[M+Na]^+$ (C18:2).

N-(2-hydroxyethyl)oleamide (RSA 4.20) (Synthesised from rapeseed oil)



The general procedure for the synthesis of ethanolamine fatty amides was applied using hydrolysed rapeseed oil (25.0 g, 89 mmol, 1.0 equiv.) and ethanolamine (8.0 mL, 132 mmol, 1.5 equiv.) to give the product as a pale yellow waxy solid. (83 %); ν_{max}/cm^{-1} 3297 (H-N, O-H), 2919 (C-H), 2850 (C-H), 1642 (C=O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H, N*H*), 5.45 – 5.25 (m, 2H, *H*C=C*H*), 3.69 (t, *J* = 5.0 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.40 (dt, *J* = 5.2 Hz, 2H, HOCH$_2$C*H*$_2$NH), 2.85 – 2.72 (m, 0.5H, HC=CHC*H*$_2$CH=CH), 2.20 (t, *J* = 7.7 Hz, 2H, O=C*H*$_2$CH$_2$), 2.13 – 1.91 (m, 4H, =CHC*H*$_2$CH$_2$), 1.68 – 1.53 (m, 2H, O=CCH$_2$C*H*$_2$), 1.28 (d, *J* = 13.5 Hz, 18H, C*H*$_2$), 0.97 (t, *J* = 7.5 Hz, 0.2H, =CHCH$_2$C*H*$_3$), 0.88 (t, *J* = 5.5 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.76 (O=*C*CH$_2$CH$_2$), 132.04 (H*C*=*C*H), 130.31 (H*C*=*C*H), 130.09 (H*C*=*C*H), 129.78 (H*C*=*C*H), 128.37 (H*C*=*C*H), 128.30 (H*C*=*C*H), 128.14 (H*C*=*C*H), 127.96 (H*C*=*C*H), 127.82 (H*C*=*C*H), 127.17 (H*C*=*C*H), 62.13 (HO*C*H$_2$CH$_2$NH), 42.43 (HOCH$_2$*C*H$_2$NH), 36.74 (O=C*C*H$_2$CH$_2$), 31.98 (CH$_2$), 29.84 (CH$_2$), 29.80 (CH$_2$), 29.71 (CH$_2$), 29.61 (CH$_2$), 29.40 (CH$_2$), 29.38 (CH$_2$), 29.24 (CH$_2$), 27.26 (=CHC*H*$_2$CH$_2$), 25.84 (HC=CH*C*H$_2$CH=CH), 25.69 (O=CCH$_2$*C*H$_2$), 22.76 (CH$_2$), 22.65 (CH$_2$), 14.37 (=CHCH$_2$*C*H$_3$), 14.21 (*C*H$_3$), 14.16 (*C*H$_3$).; *m/z* (ES^+) 348.1 $[M+Na]^+$ (C18:1), 346.1 $[M+Na]^+$ (C18:2).

N-(2-hydroxyethyl)linoleamide (SBA 4.20) (Synthesised from soybean oil)

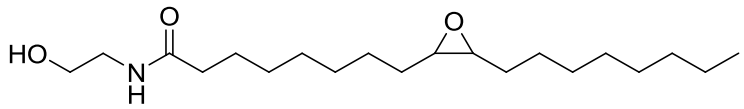


The general procedure for the synthesis of ethanolamine fatty amides was applied using hydrolysed soybean oil (25.0 g, 90 mmol, 1.0 equiv.) and ethanolamine (8.2 mL, 134 mmol, 1.5 equiv.) to give the product as a pale yellow waxy solid. (83 %); ν_{max}/cm^{-1} 3296 (H-N, O-H), 2918 (C-H), 2850 (C-H), 1642 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (s, 1H, N*H*), 5.48 – 5.24 (m, 3H, *H*C=C*H*), 3.83 (br s, 1H, O*H*), 3.69 (t, *J* = 5.0 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.39 (dt, *J* = 5.2 Hz, 2H, HOCH$_2$C*H*$_2$NH), 2.87 – 2.67 (m, 1H, HC=CHC*H*$_2$CH=CH), 2.20 (t, *J* = 7.4 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.13 – 1.91 (m, 3H, =CHC*H*$_2$CH$_2$), 1.73 – 1.49 (m, 2H, O=CCH$_2$C*H*$_2$), 1.28 (m, 18H, CH_2), 0.98 (t, *J* = 7.6 Hz, 0.3H, =CHCH$_2$C*H*$_3$), 0.94 – 0.78 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.75 (O=*C*CH$_2$CH$_2$), 132.01 (H*C*=*C*H), 130.29 (H*C*=*C*H), 130.05 (H*C*=*C*H), 129.75 (H*C*=*C*H), 128.35 (H*C*=*C*H), 128.28 (H*C*=*C*H), 128.12 (H*C*=*C*H), 127.94 (H*C*=*C*H), 127.80 (H*C*=*C*H), 127.15 (H*C*=*C*H), 62.01 (HO*C*H$_2$CH$_2$NH), 42.39 (HOCH$_2$*C*H$_2$NH), 36.71 (O=C*C*H$_2$CH$_2$), 31.96 (CH_2), 31.57 (CH_2), 29.77 (CH_2), 29.72 (CH_2), 29.70 (CH_2), 29.59 (CH_2), 29.37 (CH_2), 29.23 (CH_2), 27.25 (=C*C*H$_2$CH$_2$), 25.83 (O=CCH$_2$*C*H$_2$), 25.68 (HC=CH*C*H$_2$CH=CH), 22.75 (CH_2), 22.63 (CH_2), 14.35 (=CHCH$_2$CH$_3$), 14.18 (CH_3), 14.14 (CH_3).; *m/z* (ES^+) 348.1 $[M+Na]^+$ (C18:1), 346.1 $[M+Na]^+$ (C18:2).

6.4.9 General Procedure for the synthesis of epoxidised ethanolamine fatty amides

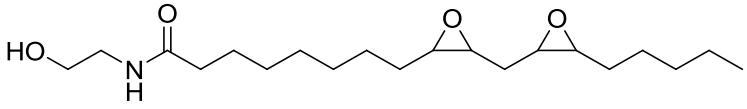
The desired fatty amide (1 equiv.) was dissolved in toluene (0.5 M) at 60 °C, Amberlite® IR 120 (25 wt%), acetic acid (0.5 equiv) and H_2O_2 (4 equiv) were added and reacted overnight at 60 °C. Amberlite® was filtered off and reaction mixture was washed with water (2x 200 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and purified through silica plug (ether followed by MeOH) to give pure product

N-(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide



The general procedure for the synthesis of epoxidised ethanolamine fatty amides was applied using **OA 4.20** (20.0 g, 62 mmol, 1.0 equiv.), Amberlite® IR 120 (5.0 g, 25 wt%) acetic acid (1.9 g, 31 mmol, 0.5 equiv) and H_2O_2 (42.0 mL, 360 mmol, 6 equiv) to give the product as a cream waxy solid. (97 %); ν_{max}/cm^{-1} 3311 (H-N, O-H), 2917 (C-H), 2849 (C-H), 1643 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (t, *J* = 4.9 Hz, 1H, N*H*), 3.68 (t, *J* = 5.0 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.39 (dt, *J* = 5.0 Hz, 2H, HOCH$_2$C*H*$_2$NH), 3.16 – 2.80 (m, 2H, CH$_2$C*H*(O)C*H*CH$_2$), 2.20 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.71 – 1.56 (m, 2H, O=CCH$_2$C*H*$_2$), 1.49 (s, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$C*H*$_2$), 1.42 – 1.17 (m, 18H, C*H*$_2$), 0.88 (t, *J* = 6.4 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.60 (O=*C*CH$_2$CH$_2$), 61.99 (HO*C*H$_2$CH$_2$NH), 57.41 (H*C*(O)*C*H), 42.35 (HOCH$_2$*C*H$_2$NH), 36.60 (O=C*C*H$_2$CH$_2$), 31.88 (*C*H$_2$), 29.56 (*C*H$_2$), 29.35 (*C*H$_2$), 29.25 (*C*H$_2$), 29.16 (*C*H$_2$), 27.84 (*C*H$_2$), 27.77 (*C*H$_2$), 26.62 (*C*H$_2$), 25.72 (O=CCH$_2$*C*H$_2$), 22.69 (*C*H$_2$), 14.15 (*C*H$_3$).; *m/z* (ES$^+$) 364.1 [M+Na]$^+$ (C18:1).

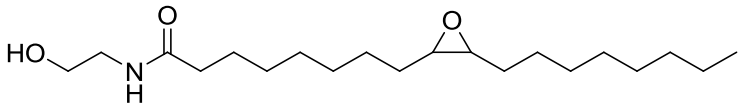
N-(2-hydroxyethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide



The general procedure for the synthesis of epoxidised ethanolamine fatty amides was applied using **LA 4.20** (20.0 g, 62 mmol, 1.0 equiv.), Amberlite® IR 120 (5.0 g, 25 wt%) acetic acid (1.9 g, 31 mmol, 0.5 equiv) and H_2O_2 (63.0 mL, 557 mmol, 9 equiv) to give the product as a cream waxy solid (70 %); ν_{max}/cm^{-1} 3312 (H-N, O-H),

2916 (C-H), 2849 (C-H), 1642 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 1H, N*H*), 3.69 (t, *J* = 5.1 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.39 (dt, *J* = 5.2 Hz, 2H, HOCH$_2$C*H*$_2$NH), 3.26 – 2.84 (m, 3H, CH$_2$C*H*(O)C*H*CH$_2$), 2.20 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.81 – 1.69 (m, 1H, (O)CHC*H*$_2$CH(O)), 1.69 – 1.58 (m, 2H, O=CCH$_2$C*H*$_2$), 1.57 – 1.43 (m, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$C*H*$_2$), 1.41 – 1.20 (m, 14H, C*H*$_2$), 0.89 (dt, *J* = 6.8 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.56 (O=*C*CH$_2$CH$_2$), 62.03 (HO*C*H$_2$CH$_2$NH), 57.41 (H*C*(O)*C*H), 57.15 (H*C*(O)*C*H), 57.12 (H*C*(O)*C*H), 56.86 (H*C*(O)*C*H), 56.82 (H*C*(O)*C*H), 54.47 (H*C*(O)*C*H), 54.43 (CH$_2$*C*H(O)*C*HCH$_2$), 54.37 (H*C*(O)*C*H), 42.35 (HOCH$_2$*C*H$_2$NH), 36.59 (O=C*C*H$_2$CH$_2$), 31.87 (*C*H$_2$), 31.68 (*C*H$_2$), 29.72 (*C*H$_2$), 29.56 (*C*H$_2$), 29.33 (*C*H$_2$), 29.24 (*C*H$_2$), 29.14 (*C*H$_2$), 27.88 (*C*H$_2$), 27.84 (*C*H$_2$), 27.77 (*C*H$_2$), 27.17 (*C*H$_2$), 26.93 (*C*H$_2$), 26.62 (*C*H$_2$), 26.47 (*C*H$_2$), 26.26 (*C*H$_2$), 26.16 (*C*H$_2$), 25.69 (*C*H$_2$), 22.69 (*C*H$_2$), 22.59 (*C*H$_2$), 14.15 (*C*H$_3$), 14.03 (*C*H$_3$).; *m/z* (ES$^+$) 378.1 [M+Na]$^+$ (C18:2), 364.1 [M+Na]$^+$ (C18:1).

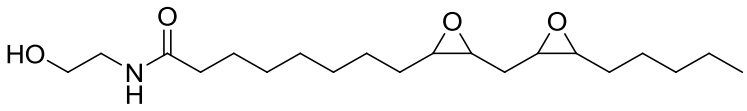
N-(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide (Synthesised from rapeseed oil)



The general procedure for the synthesis of epoxidised ethanolamine fatty amides was applied using **RSA 4.20** (20.0 g, 62 mmol, 1.0 equiv.), Amberlite® IR 120 (5.0 g, 25 wt%) acetic acid (1.9 g, 31 mmol, 0.5 equiv) and H_2O_2 (63.0 mL, 557 mmol, 9 equiv) to give the product as a cream waxy solid (70 %); ν_{max}/cm^{-1} 3312 (H-N, O-H), 2917 (C-H), 2849 (C-H), 1643 (C=O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (t, *J* = 4.6 Hz, 1H, N*H*), 3.91 (br s, 1H, O*H*), 3.68 (t, *J* = 5.0 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.38

(dt, *J* = 5.2, 4.6 Hz, 2H, $HOCH_2CH_2NH$), 3.23 – 2.85 (m, 2H, $CH_2CH(O)CHCH_2$), 2.20 (t, *J* = 7.6 Hz, 2H, $O=CCH_2CH_2$), 1.86 – 1.70 (m, 0.5H, $(O)CHCH_2CH(O)$), 1.70 – 1.57 (m, *J* = 5.6 Hz, 2H, $O=CCH_2CH_2$), 1.57 – 1.43 (m, 6H, $CH_2CH(O)CHCH_2$, $O=CCH_2CH_2CH_2$), 1.42 – 1.19 (m, 16H, CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.55 ($O=CCH_2CH_2$), 61.86 ($HOCH_2CH_2NH$), 57.37 ($HC(O)CH$), 57.35 ($HC(O)CH$), 57.11 ($HC(O)CH$), 57.07 ($HC(O)CH$), 56.81 ($HC(O)CH$), 56.77 ($HC(O)CH$), 54.42 ($HC(O)CH$), 54.38 ($HC(O)CH$), 54.34 ($HC(O)CH$), 42.31 ($HOCH_2CH_2NH$), 36.54 ($O=CCH_2CH_2$), 31.83 (CH_2), 29.68 (CH_2), 29.52 (CH_2), 29.30 (CH_2), 29.20 (CH_2), 29.12 (CH_2), 27.79 (CH_2), 27.73 (CH_2), 26.57 (CH_2), 25.68 (CH_2), 22.64 (CH_2), 14.10 (CH_3).; *m/z* (ES^+) 378.1 $[M+Na]^+$ (C18:2), 364.1 $[M+Na]^+$ (C18:1).

N-(2-hydroxyethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (Synthesised from soybean oil)



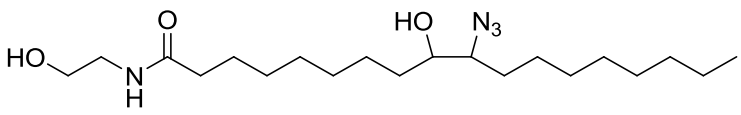
The general procedure for the synthesis of epoxidised ethanolamine fatty amides was applied using **SBA 4.20** (20.0 g, 62 mmol, 1.0 equiv.), Amberlite® IR 120 (5.0 g, 25 wt%) acetic acid (1.9 g, 31 mmol, 0.5 equiv) and H_2O_2 (63.0 mL, 557 mmol, 9 equiv) to give the product as a cream waxy solid (57 %); ν_{max}/cm^{-1} 3294 (H-N, O-H), 2917 (C-H), 2849 (C-H), 1641 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H, N*H*), 3.71 (t, *J* = 4.9 Hz, 2H, $HOCH_2CH_2NH$), 3.41 (q, *J* = 5.2 Hz, 2H, $HOCH_2CH_2NH$), 3.23 – 2.85 (m, 3H, $CH_2CH(O)CHCH_2$), 2.20 (t, *J* = 7.5 Hz, 2H, $O=CCH_2CH_2$), 1.79 – 1.70 (m, 1H, $(O)CHCH_2CH(O)$), 1.69 – 1.58 (m, 2H, $O=CCH_2CH_2$), 1.54 – 1.45 (m, 6H, $CH_2CH(O)CHCH_2$, $O=CCH_2CH_2CH_2$), 1.40 –

1.24 (m, 15H, C*H*$_2$), 0.89 (dt, *J* = 9.1, 7.1 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.60 (O=*C*CH$_2$CH$_2$), 62.48 (HO*C*H$_2$CH$_2$NH), 57.45 (H*C*(O)*C*H), 57.21 (H*C*(O)*C*H), 57.18 (H*C*(O)*C*H), 56.92 (H*C*(O)*C*H), 56.75 (H*C*(O)*C*H), 54.54 (H*C*(O)*C*H), 54.50 (H*C*(O)*C*H), 54.40 (H*C*(O)*C*H), 42.51 (HOCH$_2$*C*H$_2$NH), 36.70 (O=C*C*H$_2$CH$_2$), 32.04 (*C*H$_2$), 31.97 (*C*H$_2$), 31.78 (*C*H$_2$), 29.81 (*C*H$_2$), 29.66 (*C*H$_2$), 29.47 (*C*H$_2$), 29.34 (*C*H$_2$), 29.28 (*C*H$_2$), 29.18 (*C*H$_2$), 27.96 (*C*H$_2$), 27.86 (*C*H$_2$), 27.29 (*C*H$_2$), 27.03 (*C*H$_2$), 26.70 (*C*H$_2$), 26.53 (*C*H$_2$), 26.35 (*C*H$_2$), 26.24 (*C*H$_2$), 25.86 (*C*H$_2$), 25.73 (O=CCH$_2$*C*H$_2$), 22.77 (*C*H$_2$), 22.68 (*C*H$_2$), 14.23 (*C*H$_3$), 14.10 (*C*H$_3$).; *m/z* (ES$^+$) 378.1 [M+Na]$^+$ (C18:2), 364.1 [M+Na]$^+$ (C18:1).

6.4.10 General Procedure for the synthesis of Azido ethanolamine fatty amides

The desired epoxidised fatty amide (1 equiv.) was dissolved in ethanol:water (0.3 M, 5:1) at 100 °C. Sodium azide (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) and ammonium chloride (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) were added and reacted overnight at 100 °C. The reaction mixture was diluted with water (200 mL) and extracted with chloroform. The organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce pure product without further purification.

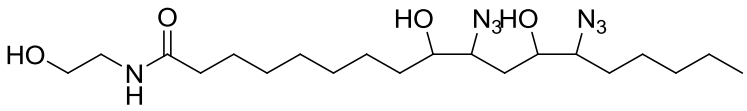
10-Azido-9-hydroxy-N-(2-hydroxyethyl)octadecanamide (AzOA 4.21)



The general procedure for the synthesis of azido ethanolamine fatty amides was applied using **epoxy OA 4.20** (19.9 g, 58 mmol, 1.0 equiv.), NaN_3 (7.6 g, 117 mmol, 2.0 equiv.) and NH_4Cl (6.2 g, 117 mmol, 2.0 equiv) to give the product as an orange

oil. (74 %); ν_{max}/cm^{-1} 3306 (H-N, O-H), 2923 (C-H), 2853 (C-H), 2098 ($N=N^+=N^-$), 1645 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 – 6.31 (m, 1H, N*H*), 3.70 (t, J = 4.9 Hz, 2H, HOC*H*$_2$CH$_2$NH), 3.54 (dt, J = 8.4, 4.7 Hz, 1H, CH$_2$C*H*(OH)), 3.40 (dt, J = 5.1 Hz, 2H, HOCH$_2$C*H*$_2$NH), 3.18 (dt, J = 13.0, 4.9 Hz, 1H, (N$_3$)C*H*CH$_2$), 2.20 (t, J = 7.5 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.71 – 1.57 (m, 4H, (N$_3$)CHC*H*$_2$, O=CC*H*$_2$CH$_2$), 1.56 – 1.38 (m, 4H, C*H*$_2$CH(OH), C*H*$_2$), 1.39 – 1.19 (m, 18H, C*H*$_2$), 0.88 (t, J = 6.4 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.74 (O=*C*CH$_2$CH$_2$), 74.62 (CH$_2$*C*H(OH)), 74.54 (CH$_2$*C*H(OH)), 73.97 (CH$_2$*C*H(OH)), 73.60 (CH$_2$*C*H(OH)), 67.32 ((N$_3$)*C*HCH$_2$), 67.09 ((N$_3$)*C*HCH$_2$), 62.23 (HO*C*H$_2$CH$_2$NH), 62.20 (HO*C*H$_2$CH$_2$NH), 42.43 (HOCH$_2$*C*H$_2$NH), 42.40 (HOCH$_2$*C*H$_2$NH), 36.65 (O=C*C*H$_2$CH$_2$), 34.35 (*C*H$_2$), 34.24 (*C*H$_2$), 31.96 (*C*H$_2$), 30.94 (*C*H$_2$), 30.83 (*C*H$_2$), 29.80 (*C*H$_2$), 29.70 (*C*H$_2$), 29.63 (*C*H$_2$), 29.57 (*C*H$_2$), 29.36 (*C*H$_2$), 29.33 (*C*H$_2$), 29.29 (*C*H$_2$), 29.13 (*C*H$_2$), 29.01 (*C*H$_2$), 26.39 (*C*H$_2$), 26.23 (*C*H$_2$), 25.80 (*C*H$_2$), 25.70 (*C*H$_2$), 25.67 (*C*H$_2$), 25.54 (*C*H$_2$), 22.76 (*C*H$_2$), 14.23 (*C*H$_3$).; *m/z* (ES^+) 407.3 $[M+Na]^+$ (C18:1).

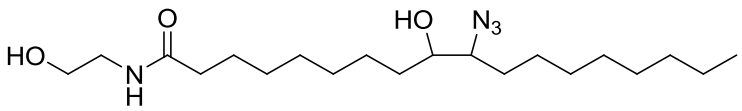
10,13-Diazido-9,12-dihydroxy-N-(2-hydroxyethyl)octadecanamide (AzLA 4.21)



The general procedure for the synthesis of azido ethanolamine fatty amides was applied using **epoxy LA 4.20** (14.0 g, 32 mmol, 1.0 equiv.), NaN_3 (8.2 g, 127 mmol, 4.0 equiv.) and NH_4Cl (6.8 g, 127 mmol, 4.0 equiv) to give the product as an orange oil. (90 %); ν_{max}/cm^{-1} 3301 (H-N, O-H), 2923 (C-H), 2853 (C-H), 2098 ($N=N^+=N^-$), 1640 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.70 – 6.38 (m, 1H, N*H*), 3.72 – 3.65 (m, 2H, HOC*H*$_2$CH$_2$NH), 3.63 – 3.49 (m, 1.5H, CH$_2$C*H*(OH)), 3.42 – 3.35 (m, 2H,

$HOCH_2CH_2NH$), 3.28 – 3.03 (m, 1.5H, $(N_3)CHCH_2$), 2.21 (t, *J* = 7.3 Hz, 2H, $O=CCH_2CH_2$), 1.72 – 1.57 (m, 5H, $(N_3)CHCH_2$, $O=CCH_2CH_2$), 1.57 – 1.39 (m, 4H, $CH_2CH(OH)$, CH_2), 1.39 – 1.17 (m, 14H, CH_2), 0.89 (dt, *J* = 13.2, 6.5 Hz, 3H, $(N_3)CHCH_3$, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.94 ($O=CCH_2CH_2$), 74.63 ($CH_2CH(OH)$), 74.43 ($CH_2CH(OH)$), 74.27 ($CH_2CH(OH)$), 73.80 ($CH_2CH(OH)$), 73.63 ($CH_2CH(OH)$), 73.17 ($CH_2CH(OH)$), 72.92 ($CH_2CH(OH)$), 70.64 ($CH_2CH(OH)$), 70.52 ($CH_2CH(OH)$), 70.29 ($CH_2CH(OH)$), 69.74 ($CH_2CH(OH)$), 67.71 ($(N_3)CHCH_2$), 67.52 ($(N_3)CHCH_2$), 67.30 ($(N_3)CHCH_2$), 67.20 ($(N_3)CHCH_2$), 67.06 ($(N_3)CHCH_2$), 66.87 ($(N_3)CHCH_2$), 66.68 ($(N_3)CHCH_2$), 63.71 ($(N_3)CHCH_2$), 62.09 ($HOCH_2CH_2NH$), 61.92 ($HOCH_2CH_2NH$), 42.37 ($HOCH_2CH_2NH$), 36.62 ($O=CCH_2CH_2$), 34.34 (CH_2), 34.22 (CH_2), 31.93 (CH_2), 31.83 (CH_2), 31.71 (CH_2), 30.94 (CH_2), 30.82 (CH_2), 30.56 (CH_2), 30.37 (CH_2), 30.26 (CH_2), 29.69 (CH_2), 29.62 (CH_2), 29.56 (CH_2), 29.35 (CH_2), 29.29 (CH_2), 29.12 (CH_2), 29.08 (CH_2), 29.01 (CH_2), 28.94 (CH_2), 28.80 (CH_2), 26.39 (CH_2), 26.24 (CH_2), 26.02 (CH_2), 25.80 (CH_2), 25.67 (CH_2), 25.55 (CH_2), 22.75 (CH_2), 22.67 (CH_2), 22.61 (CH_2), 14.22 ($(N_3)CHCH_3$), 14.14 (CH_3), 14.11 (CH_3).; *m/z* (ES^+) 464.3 $[M+Na]^+$ (C18:2), 407.3 $[M+Na]^+$ (C18:1).

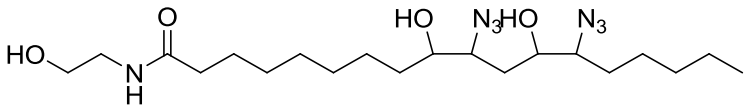
10-Azido-9-hydroxy-N-(2-hydroxyethyl)octadecanamide (AzRSA 4.21) (Synthesised from rapeseed oil)



The general procedure for the synthesis of azido ethanolamine fatty amides was applied using **epoxy RSA 4.20** (14.8 g, 42 mmol, 1.0 equiv.), NaN_3 (8.1 g, 124 mmol, 3.0 equiv.) and NH_4Cl (6.7 g, 124 mmol, 3.0 equiv) to give the product as an

orange oil. (85 %); ν_{max}/cm^{-1} 3322 (H-N, O-H), 2924 (C-H), 2855 (C-H), 2098 ($N=N^+=N^-$), 1641 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.41 (m, 1H, N*H*), 3.68 (t, J = 4.9 Hz, 2H, HOCH_2CH_2NH), 3.58 – 3.49 (m, 1H, CH_2C*H*(OH)), 3.39 (dt, J = 4.7 Hz, 2H, HOCH_2CH_2NH), 3.22 – 3.13 (m, 1H, (N_3)C*H*CH_2), 2.20 (t, J = 7.3 Hz, 2H, O=CCH_2CH_2), 1.72 – 1.55 (m, 4H, (N_3)CHCH_2, O=CCH_2CH_2), 1.55 – 1.38 (m, 4H, CH_2CH(OH), CH_2), 1.39 – 1.09 (m, 17H, CH_2), 0.88 (t, J = 6.6 Hz, 3H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.82 (O=*C*CH_2CH_2), 73.60 (CH_2*C*H(OH)), 73.57 (CH_2*C*H(OH)), 67.26 ((N_3)*C*HCH_2), 67.01 ((N_3)*C*HCH_2), 61.95 (HO*C*H_2CH_2NH), 61.93 (HO*C*H_2CH_2NH), 42.33 (HOCH_2*C*H_2NH), 36.59 (O=C*C*H_2CH_2), 34.29 (*C*H_2), 34.19 (*C*H_2), 31.99 (*C*H_2), 31.92 (*C*H_2), 31.91 (*C*H_2), 30.89 (*C*H_2), 30.77 (*C*H_2), 29.77 (*C*H_2), 29.72 (*C*H_2), 29.68 (*C*H_2), 29.60 (*C*H_2), 29.54 (*C*H_2), 29.43 (*C*H_2), 29.33 (*C*H_2), 29.29 (*C*H_2), 29.10 (*C*H_2), 28.98 (*C*H_2), 26.38 (*C*H_2), 26.23 (*C*H_2), 25.79 (*C*H_2), 25.69 (*C*H_2), 25.66 (*C*H_2), 25.54 (*C*H_2), 22.72 (*C*H_2), 14.19 (*C*H_3), 14.08 (*C*H_3).; *m/z* (ES^+) 464.3 $[M+Na]^+$ (C18:2), 407.3 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxy-N-(2-hydroxyethyl)octadecanamide (AzSBA 4.21) (Synthesised from soybean oil)



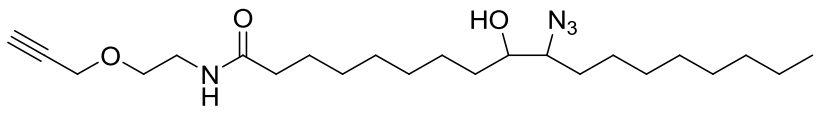
The general procedure for the synthesis of azido ethanolamine fatty amides was applied using **epoxy SBA 4.20** (12.0 g, 34 mmol, 1.0 equiv.), NaN_3 (8.8 g, 135 mmol, 4.0 equiv.) and NH_4Cl (7.3 g, 135 mmol, 4.0 equiv) to give the product as an orange oil. (64 %); ν_{max}/cm^{-1} 3296 (H-N, O-H), 2918 (C-H), 2850 (C-H), 2101 ($N=N^+=N^-$), 1640 (C=O).; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 – 6.10 (m, 1H, N*H*),

4.27 – 3.74 (m, 1H, $CH_2CH(OH)$, $(N_3)CHCH_2$), 3.71 (t, J = 4.4 Hz, 2H, $HOCH_2CH_2NH$), 3.65 – 3.45 (m, 1H, $CH_2CH(OH)$), 3.45 – 3.35 (m, 2H, $HOCH_2CH_2NH$), 3.34 – 3.09 (m, 1H, $(N_3)CHCH_2$), 2.20 (t, J = 7.6 Hz, 2H, $O=CCH_2CH_2$), 1.72 – 1.56 (m, 4H, $(N_3)CHCH_2$, $O=CCH_2CH_2$), 1.56 – 1.41 (m, 4H, $CH_2CH(OH)$, CH_2), 1.41 – 1.19 (m, 16H, CH_2), 0.88 (td, J = 6.9, 3.9 Hz, 3H, $(N_3)CHCH_3$, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.81 ($O=CCH_2CH_2$), 84.38 ($(N_3)CHCH_2$), 82.78 ($CH_2CH(OH)$), 80.49 ($CH_2CH(OH)$), 80.31 ($(N_3)CHCH_2$), 79.45 ($CH_2CH(OH)$), 74.58 ($CH_2CH(OH)$), 74.36 ($CH_2CH(OH)$), 74.28 ($CH_2CH(OH)$), 73.92 ($(N_3)CHCH_2$), 73.63 ($CH_2CH(OH)$), 73.27 ($CH_2CH(OH)$), 71.52 ($(N_3)CHCH_2$), 67.15 ($(N_3)CHCH_2$), 62.49 ($HOCH_2CH_2NH$), 62.27 ($HOCH_2CH_2NH$), 42.53 ($HOCH_2CH_2NH$), 42.42 ($HOCH_2CH_2NH$), 36.81 ($O=CCH_2CH_2$), 32.05 (CH_2), 29.82 (CH_2), 29.63 (CH_2), 29.49 (CH_2), 29.42 (CH_2), 29.31 (CH_2), 29.15 (CH_2), 29.06 (CH_2), 28.88 (CH_2), 28.74 (CH_2), 26.03 (CH_2), 25.86 (CH_2), 25.68 (CH_2), 22.78 (CH_2), 14.26 ($(N_3)CHCH_3$), 14.19 (CH_3).; *m/z* (ES^+) 464.3 $[M+Na]^+$ (C18:2), 407.3 $[M+Na]^+$ (C18:1).

6.4.11 General Procedure for the synthesis of propargyl azido ethanolamine fatty amides

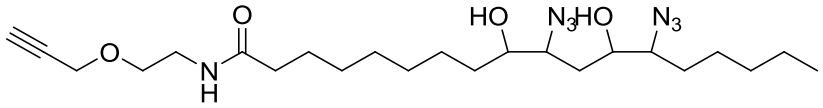
The desired azido ethanolamine fatty amide (1.0 equiv.) was dissolved in dry THF (0.5 M) at -78 °C, NaH (60 %) (1.05 equiv.) was added and left for 30 mins. Propargyl bromide (80 wt. % in toluene) (1.2 equiv.) was added dropwise and left to warm to room temperature overnight. The reaction mixture was quenched with aqueous acid (20 mL 2 M HCl) and extracted using Et_2O. The organic layer was washed with water (2 x 50 mL) then saturated NaCl (50 mL and dried over $MgSO_4$. The solvent was removed *in vacuo* to give crude product which was purified through silica plug (8:1) (Et_2O:Hex) to give pure product.

10-Azido-9-hydroxy-N-(2-(prop-2-ynyloxy)ethyl)octadecanamide (EtOA 4.10)



The general procedure for the synthesis of propargyl azido ethanolamine fatty amides was applied using **AzOA 4.21** (16.0 g, 42 mmol, 1.0 equiv.), NaH (1.8 g, 44 mmol, 1.05 equiv) and propargyl bromide (5.1 mL, 46 mmol, 1.1 equiv.) to give the product as a pale yellow oil. (65 %); ν_{max}/cm^{-1} 3311 (N-H, O-H, ≡C-H), 2924 (C-H), 2854 (C-H) 2100 ($N=N^+=N^-$), 1647 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (s, 1H, N*H*), 4.16 (d, *J* = 2.4 Hz, 2H, HC≡CC*H*$_2$O), 3.60 (t, *J* = 5.1 Hz, 2H, OC*H*$_2$CH$_2$N), 3.58 – 3.51 (m, 1H, (HO)C*H*CH$_2$), 3.47 (t, *J* = 5.9 Hz, 2H, OCH$_2$C*H*$_2$N), 3.21 – 3.12 (m, 1H, CH$_2$C*H*(N$_3$)), 2.49 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH$_2$O), 2.18 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.68 – 1.57 (m, 4H, C*H*$_2$CH(N$_3$), O=CCH$_2$C*H*$_2$), 1.53 – 1.48 (m, 2H, (HO)CHC*H*$_2$), 1.39 – 1.23 (m, 20H, C*H*$_2$), 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.43 (O=CCH$_2$CH$_2$), 79.29 (H*C*≡CCH$_2$O), 74.82 (HC≡*C*CH$_2$O), 73.44 ((HO)*C*HCH$_2$), 73.39 ((HO)*C*HCH$_2$), 68.77 (O*C*H$_2$CH$_2$N), 67.04 (CH$_2$*C*H(N$_3$)), 66.94 (CH$_2$*C*H(N$_3$)), 58.20 (HC≡C*C*H$_2$O), 39.00 (OCH$_2$*C*H$_2$N), 36.54 (O=CCH$_2$CH$_2$), 34.07 ((HO)CH*C*H$_2$), 31.82 (*C*H$_2$), 31.80 (*C*H$_2$), 31.54 (*C*H$_2$), 30.70 (*C*H$_2$), 30.64 ((N$_3$)CH*C*H$_2$), 29.65 (*C*H$_2$), 29.58 (*C*H$_2$), 29.51 (*C*H$_2$), 29.43 (*C*H$_2$), 29.32 (*C*H$_2$), 29.23 (*C*H$_2$), 29.19 (*C*H$_2$), 29.12 (*C*H$_2$), 29.07 (*C*H$_2$), 26.84 (*C*H$_2$), 26.29 (*C*H$_2$), 26.20 (*C*H$_2$), 25.76 (*C*H$_2$), 25.67 (*C*H$_2$), 25.58 (*C*H$_2$), 25.55 (*C*H$_2$), 25.21 (O=CCH$_2$*C*H$_2$), 22.60 (*C*H$_2$), 22.54 (*C*H$_2$), 14.26 (*C*H$_3$), 14.06 (*C*H$_3$).; *m/z* (ES^+) 445.3 $[M+Na]^+$ (C18:1).

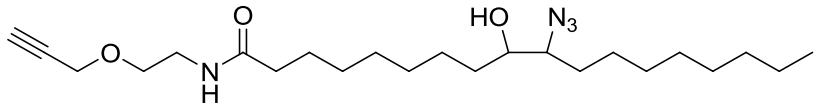
10,13-Diazido-9,12-dihydroxy-N-(2-(prop-2-ynyloxy)ethyl)octadecanamide (EtLA 4.10)



The general procedure for the synthesis of propargyl azido ethanolamine fatty amides was applied using **AzLA 4.21** (15.6 g, 35 mmol, 1.0 equiv.), NaH (2.1 g, 53 mmol, 1.05 equiv) and propargyl bromide (4.3 mL, 46 mmol, 1.1 equiv.) to give the product as a pale yellow oil. (44 %); ν_{max}/cm^{-1} 3306 (N-H, O-H, ≡C-H), 2925 (C-H), 2855 (C-H) 2101 ($N=N^{+}=N^{-}$), 1648 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H, N*H*), 4.16 (d, *J* = 2.3 Hz, 2H, HC≡CC*H*$_2$O), 3.88 – 3.64 (m, 1H, (HO)C*H*CH$_2$, CH$_2$C*H*(N$_3$)), 3.63 – 3.58 (m, 2H, OC*H*$_2$CH$_2$N), 3.57 – 3.51 (m, 1H, (HO)C*H*CH$_2$), 3.50 – 3.43 (m, 2H, OCH$_2$C*H*$_2$N), 3.26 – 3.11 (m, 1H, CH$_2$C*H*(N$_3$)), 2.48 (t, *J* = 2.4 Hz, 1H, *H*C≡CCH$_2$O), 2.18 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.67 – 1.58 (m, 4H, O=CC*H*$_2$CH$_2$, C*H*$_2$CH(N$_3$)), 1.54 – 1.46 (m, 2H, (HO)CHC*H*$_2$), 1.41 – 1.24 (m, 18H, C*H*$_2$), 0.90 – 0.86 (m, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.45 (O=*C*CH$_2$CH$_2$), 79.33 (H*C*≡CCH$_2$O), 74.85 (HC≡*C*CH$_2$O), 73.76 ((HO)*C*HCH$_2$), 73.49 ((HO)*C*HCH$_2$), 73.44 ((HO)*C*HCH$_2$), 72.96 ((HO)*C*HCH$_2$), 72.70 ((HO)*C*HCH$_2$), 70.44 ((HO)*C*HCH$_2$), 70.36 ((HO)*C*HCH$_2$), 70.20 ((HO)*C*HCH$_2$), 69.98 ((HO)*C*HCH$_2$), 68.79 (O*C*H$_2$CH$_2$N), 67.56 (CH$_2$C*H*(N$_3$)), 67.33 (CH$_2$C*H*(N$_3$)), 67.13 (CH$_2$C*H*(N$_3$)), 67.02 (CH$_2$C*H*(N$_3$)), 66.82 (CH$_2$C*H*(N$_3$)), 66.69 (CH$_2$C*H*(N$_3$)), 58.26 (HC≡C*C*H$_2$O), 39.05 (OCH$_2$*C*H$_2$N), 36.62 O=C*C*H$_2$CH$_2$), 34.14 ((HO)CH*C*H$_2$), 31.84 (*C*H$_2$), 31.82 (*C*H$_2$), 31.74 (*C*H$_2$), 31.57 (*C*H$_2$), 30.78 (*C*H$_2$), 30.73 (*C*H$_2$), 30.65 ((N$_3$)CH*C*H$_2$), 29.67 (*C*H$_2$), 29.59 (*C*H$_2$), 29.51 (*C*H$_2$), 29.45 (*C*H$_2$), 29.31 (*C*H$_2$), 29.25 (*C*H$_2$), 29.21 (*C*H$_2$), 29.13 (*C*H$_2$), 29.08 (*C*H$_2$), 28.97 (*C*H$_2$), 26.88 (*C*H$_2$), 26.28 (*C*H$_2$), 26.20 (*C*H$_2$), 25.91 (*C*H$_2$), 25.67 (*C*H$_2$),

25.60 (CH_2), 25.54 (CH_2), 25.25 (O=CCH_2CH_2), 22.64 (CH_2), 22.57 (CH_2), 22.50 (CH_2), 14.11 (CH_3), 13.99 (CH_3). *m/z* (ES^+) 502.3 $[M+Na]^+$ (C18:2), 445.3 $[M+Na]^+$ (C18:1).

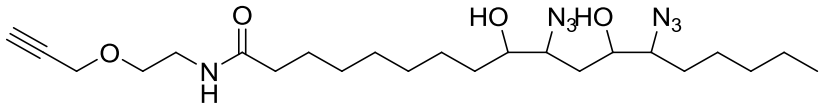
10-Azido-9-hydroxy-N-(2-(prop-2-ynyloxy)ethyl)octadecanamide (EtRSA 4.10) (Synthesised from rapeseed oil)



The general procedure for the synthesis of propargyl azido ethanolamine fatty amides was applied using **AzRSA 4.21** (15.7 g, 35 mmol, 1.0 equiv.), NaH (2.2 g, 53 mmol, 1.05 equiv) and propargyl bromide (7.9 mL, 70 mmol, 1.1 equiv.) to give the product as a pale yellow oil. (68 %); ν_{max}/cm^{-1} 3296 (N-H, O-H, ≡C-H), 2919 (C-H), 2851 (C-H) 2099 ($N=N^+=N^-$) 1637 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H, N*H*), 4.16 (d, J = 2.3 Hz, 2H, HC≡CCH_2O), 3.60 (t, J = 5.1 Hz, 2H, HOCH_2CH_2NH), 3.57 – 3.51 (m, 1H, CH_2CH(OH)), 3.47 (dt, J = 5.4 Hz, 2H, $HOCH_2CH_2$NH), 3.17 (dt, J = 4.4, 6.8 Hz, 1H, $(N_3)CHCH_2$), 2.49 (t, J = 2.3 Hz, 1H *H*C≡CCH_2O), 2.18 (t, J = 7.6 Hz, 2H, O=CCH_2CH_2), 1.72 – 1.56 (m, 4H, $(N_3)CHCH_2$, O=CCH_2CH_2), 1.55 – 1.40 (m, 4H, CH_2CH(OH), CH_2), 1.40 – 1.21 (m, 17H, CH_2), 0.88 (t, J = 6.5 Hz, 3H CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.36 (O=*C*CH_2CH_2), 79.35 (H*C*≡CCH_2O), 76.24 (CH_2*C*H(OH)), 74.83 (HC≡*C*CH_2O), 73.46 (CH_2*C*H(OH)), 73.41 (CH_2*C*H(OH)), 68.79 (HO*C*H_2CH_2NH), 67.07 ((N_3)*C*HCH_2), 66.97 ((N_3)*C*HCH_2), 58.23 (HC≡C*C*H_2O), 39.01 ($HOCH_2$*C*H_2NH), 36.59 (O=C*C*H_2CH_2), 34.18 (*C*H_2), 34.11 ((HO)CH*C*H_2), 31.83 (*C*H_2), 31.80 (*C*H_2), 31.54 (*C*H_2), 30.73 (*C*H_2), 30.67 ($(N_3)CH$*C*H_2), 29.65 (*C*H_2), 29.62 (*C*H_2), 29.58 (*C*H_2), 29.50 (*C*H_2), 29.43 (*C*H_2), 29.32 (*C*H_2), 29.23 (*C*H_2), 29.19 (*C*H_2), 29.13

(CH_2), 29.09 (CH_2), 26.28 (CH_2), 26.20 (CH_2), 25.67 (CH_2), 25.59 (CH_2), 25.55 (CH_2), 22.62 (CH_2), 14.09 (CH_3).; *m/z* (ES^+) 502.3 $[M+Na]^+$ (C18:2), 445.3 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxy-N-(2-(prop-2-ynyloxy)ethyl)octadecanamide (EtSBA 4.10) (Synthesised from soybean oil)



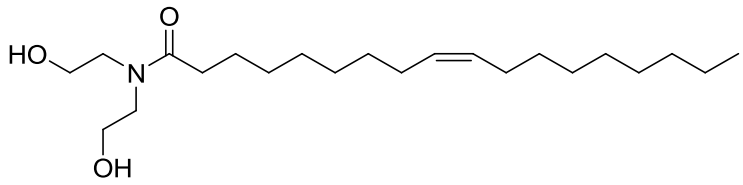
The general procedure for the synthesis of propargyl azido ethanolamine fatty amides was applied using **AzSBA 4.21** (17.8 g, 40 mmol, 1.0 equiv.), NaH (1.7 g, 42 mmol, 1.05 equiv) and propargyl bromide (4.9 mL, 44 mmol, 1.1 equiv.) to give the product as a pale yellow oil. (46 %); ν_{max}/cm^{-1} 3303 (N-H, O-H, ≡C-H), 2924 (C-H), 2854 (C-H) 2099 ($N=N^+=N^-$), 1645 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1H, N*H*), 4.16 (d, J = 2.3 Hz, 2H, HC≡CCH_2O), 4.12 – 3.74 (m, 1.5H, CH_2CH(OH), (N_3)C*H*CH_2), 3.60 (t, J = 5.1 Hz, 2H, HOCH_2CH_2NH), 3.57 – 3.51 (m, 1H, CH_2CH(OH)), 3.46 (dt, J = 5.3 Hz, 2H, $HOCH_2CH_2$NH), 3.22 – 3.12 (m, 1H, (N_3)C*H*CH_2), 2.50 (t, J = 2.5 Hz, 1H, *H*C≡CCH_2O), 2.19 (t, J = 7.5 Hz, 2H, O=CCH_2CH_2), 1.67 – 1.58 (m, 4H, (N_3)CHCH_2, O=CCH_2CH_2), 1.57 – 1.41 (m, 4H, CH_2CH(OH), CH_2), 1.37 – 1.24 (m, 16H, CH_2), 0.89 (dt, J = 7.0, 6.3, 4.3 Hz, 3H, (N_3)CHCH_3, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54 (O=*C*CH_2CH_2), 79.27 (H*C*≡CCH_2O), 74.83 (HC≡*C*CH_2O), 73.40 (CH_2*C*H(OH)), 73.35 (CH_2*C*H(OH)), 72.81 (CH_2*C*H(OH)), 72.60 (CH_2*C*H(OH)), 70.38 (CH_2*C*H(OH)), 70.33 (CH_2*C*H(OH)), 70.07 (CH_2*C*H(OH)), 69.92 (CH_2*C*H(OH)), 68.65 (HO*C*H_2CH_2NH), 67.47 ((N_3)*C*HCH_2), 67.39 ((N_3)*C*HCH_2), 67.19 ((N_3)*C*HCH_2), 67.06 ((N_3)*C*HCH_2), 66.96 ((N_3)*C*HCH_2), 66.86 ((N_3)*C*HCH_2), 66.61 ((N_3)*C*HCH_2), 66.50 ((N_3)*C*HCH_2),

63.51 ($(N_3)CHCH_2$), 63.44 ($(N_3)CHCH_2$), 58.15 ($HC{\equiv}CCH_2O$), 38.99 ($HOCH_2CH_2NH$), 36.48 ($O{=}CCH_2CH_2$), 34.08 ($(HO)CHCH_2$), 34.01 (CH_2), 33.93 (CH_2), 31.81 (CH_2), 31.75 (CH_2), 31.73 (CH_2), 31.68 (CH_2), 31.53 (CH_2), 30.64 ($(N_3)CHCH_2$), 30.59 (CH_2), 30.54 (CH_2), 30.45 (CH_2), 30.37 (CH_2), 30.31 (CH_2), 30.23 (CH_2), 30.00 (CH_2), 29.58 (CH_2), 29.52 (CH_2), 29.44 (CH_2), 29.36 (CH_2), 29.25 (CH_2), 29.17 (CH_2), 29.12 (CH_2), 29.06 (CH_2), 29.01 (CH_2), 28.96 (CH_2), 28.91 (CH_2), 26.22 (CH_2), 26.15 (CH_2), 25.95 (CH_2), 25.84 (CH_2), 25.65 (CH_2), 25.61 (CH_2), 25.53 (CH_2), 25.49 (CH_2), 22.55 (CH_2), 22.50 (CH_2), 22.42 (CH_2), 14.03 ($(N_3)CHCH_3$), 13.93 (CH_3).; *m/z* (ES^+) 502.3 $[M+Na]^+$ (C18:2), 445.3 $[M+Na]^+$ (C18:1).

6.4.12 General Procedure for the synthesis of diethanolamine fatty amides

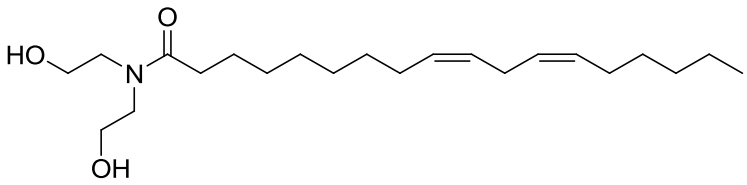
The desired fatty acid (1.0 equiv.) was dissolved in THF (0.7 M) at 0 °C, N-methylmorpholine (1.1 equiv.) was added and left for 5 mins followed by ethyl chloroformate (1.1 equiv.) added dropwise and the reaction mixture was then left for 30 mins. NMM hydrochloride was filtered off and mixed anhydride solution added dropwise to a stirred solution of diethanolamine (1.1 equiv.) and TEA (1.1 equiv.) in DMF (0.7 M) at RT. The reaction mixture was stirred for 2 hours at room temperature followed by quenching with aqueous acid (20 mL 2 M HCl). The reaction mixture was extracted using Et_2O. The organic layer was washed with water (2 x 50 mL) then saturated NaCl (50 mL and dried over $MgSO_4$. The solvent was removed *in vacuo* to give crude product which was purified through silica plug (6:1) (pet ether: EtOAc) to give pure product.

N,N-bis(2-hydroxyethyl)oleamide (OA 4.22)



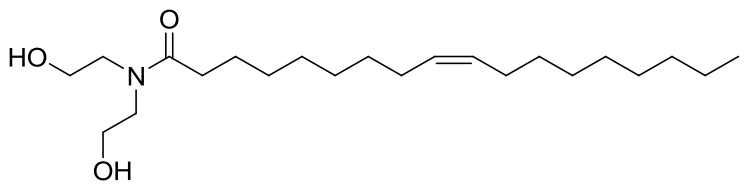
The general procedure for the synthesis of diethanolamine fatty amides was applied using oleic acid **1.22** (30.0 g, 106 mmol, 1.0 equiv.), NMM (12.8 mL, 116 mmol, 1.1 equiv.) and ethyl chloroformate (11.2 mL, 116 mmol, 1.1 equiv.) followed by diethanolamine (11.2 g, 116 mmol, 1.1 equiv) and TEA (16.3 mL, 116 mmol, 1.1 equiv) to give the product as a yellow oil. (79 %); ν_{max}/cm^{-1} 3355 (O-H), 2921 (C-H), 2852 (C-H) 1617 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.32 (m, 2H, *H*C=C*H*), 5.04 (s, 2H, O*H*), 3.80 – 3.69 (m, 4H, HOC*H*$_2$CH$_2$N), 3.50 (dt, *J* = 13.3, 5.1 Hz, 4H, HOCH$_2$C*H*$_2$N), 2.38 (t, *J* = 7.9 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.04 – 1.97 (m, 4H, =CHC*H*$_2$CH$_2$), 1.63 – 1.54 (m, 2H, O=CCH$_2$C*H*$_2$), 1.33 – 1.26 (m, 20H, C*H*$_2$), 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.62 (O=*C*CH$_2$CH$_2$), 130.14 (H*C*=*C*H), 129.93 (H*C*=*C*H), 129.67 (H*C*=*C*H), 128.01 (H*C*=*C*H), 127.87 (H*C*=*C*H), 60.80 (HO*C*H$_2$CH$_2$N), 60.50 (HO*C*H$_2$CH$_2$N), 52.13 (HOCH$_2$*C*H$_2$N), 50.36 (HOCH$_2$*C*H$_2$N), 33.55 (O=C*C*H$_2$CH$_2$), 31.88 (*C*H$_2$), 29.74 (*C*H$_2$), 29.64 (*C*H$_2$), 29.51 (*C*H$_2$), 29.43 (*C*H$_2$), 29.42 (*C*H$_2$), 29.30 (*C*H$_2$), 29.23 (*C*H$_2$), 27.19 (=CH*C*H$_2$CH$_2$), 25.45 (O=CCH$_2$*C*H$_2$), 25.33 (*C*H$_2$), 22.65 (*C*H$_2$), 14.08 (*C*H$_3$).; *m/z* (ES^+) 392.1 $[M+Na]^+$ (C18:1).

N,N-bis(2-hydroxyethyl)linoleamide (LA 4.22)



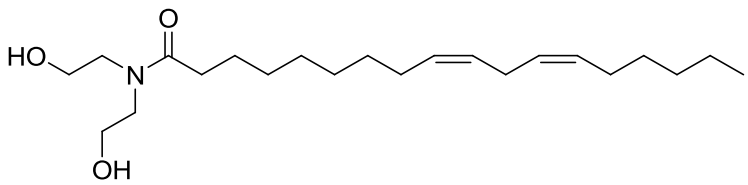
The general procedure for the synthesis of diethanolamine fatty amides was applied using linoleic acid **1.23** (30.0 g, 107 mmol, 1.0 equiv.), NMM (12.9 mL, 118 mmol, 1.1 equiv.) and ethyl chloroformate (11.3 mL, 118 mmol, 1.1 equiv.) followed by diethanolamine (11.3 g, 116 mmol, 1.1 equiv) and TEA (16.4 mL, 116 mmol, 1.1 equiv) to give the product as a yellow oil. (91 %); ν_{max}/cm^{-1} 3358 (O-H), 2922 (C-H), 2852 (C-H) 1617 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.30 (m, 3H, *H*C=C*H*), 4.82 (s, 2H, O*H*), 3.79 – 3.68 (m, 4H, HOCH_2CH_2N), 3.59 – 3.38 (m, 4H, HOCH_2CH_2N), 2.83 – 2.69 (m, 1H, HC=CHCH_2CH=CH), 2.38 (t, *J* = 7.7 Hz, 2H, O=CCH_2CH_2), 2.09 – 1.97 (m, 4H, =CHCH_2CH_2), 1.66 – 1.51 (m, 2H, , O=CCH_2CH_2), 1.34 – 1.26 (m, 16H, CH_2), 1.04 – 0.82 (m, 3H, =CHCH_2CH_3, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.37 (O=*C*CH_2CH_2), 130.05 (H*C*=*C*H), 129.86 (H*C*=*C*H), 129.68 (H*C*=*C*H), 129.58 (H*C*=*C*H), 128.15 (H*C*=*C*H), 128.10 (H*C*=*C*H), 127.93 (H*C*=*C*H), 127.79 (H*C*=*C*H), 127.61 (H*C*=*C*H), 60.62 (HO*C*H$_2$CH$_2$N), 60.37 (HO*C*H$_2$CH$_2$N), 51.98 (HOCH$_2$*C*H$_2$N), 50.21 (HOCH$_2$*C*H$_2$N), 33.44 (O=C*C*H$_2$CH$_2$), 31.80 (*C*H$_2$), 31.40 (*C*H$_2$), 29.66 (*C*H$_2$), 29.56 (*C*H$_2$), 29.42 (*C*H$_2$), 29.34 (*C*H$_2$), 29.23 (*C*H$_2$), 29.21 (*C*H$_2$), 29.14 (*C*H$_2$), 27.11 (*C*H$_2$), 27.08 (*C*H$_2$), 25.52 (HC=CH*C*H$_2$CH=CH), 25.25 (*C*H$_2$), 22.57 (*C*H$_2$), 22.46 (*C*H$_2$), 14.00 (*C*H$_3$), 13.96 (=CHCH$_2$*C*H$_3$).; *m/z* (ES$^+$) 392.1 [M+Na]$^+$ (C18:1), 390.1 [M+Na]$^+$ (C18:2).

N,N-bis(2-hydroxyethyl)oleamide (RSA 4.22) (Synthesised from rapeseed oil)



The general procedure for the synthesis of diethanolamine fatty amides was applied using hydrolysed rapeseed oil (30.0 g, 106 mmol, 1.0 equiv.), NMM (12.9 mL, 117 mmol, 1.1 equiv.) and ethyl chloroformate (11.2 mL, 117 mmol, 1.1 equiv.) followed by diethanolamine (11.2 g, 117 mmol, 1.1 equiv) and TEA (16.3 mL, 116 mmol, 1.1 equiv) to give the product as a yellow oil. (80 %); ν_{max}/cm^{-1} 3357 (O-H), 2921 (C-H), 2852 (C-H) 1617 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.26 (m, 2.5H, *H*C=C*H*), 4.57 (s, 2H, O*H*), 3.77 (dt, *J* = 13.8, 5.1 Hz, 4H, HOC*H*$_2$CH$_2$N), 3.50 (dt, *J* = 15.5, 5.1 Hz, 4H, HOCH$_2$C*H*$_2$N), 2.84 – 2.73 (m, 0.5H, HC=CHC*H*$_2$CH=CH), 2.38 (t, *J* = 7.9 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.10 – 1.95 (m, 4H, =CHC*H*$_2$CH$_2$), 1.66 – 1.53 (m, 2H, O=CCH$_2$C*H*$_2$), 1.35 – 1.24 (m, 20H, C*H*$_2$), 0.99 – 0.83 (m, 3H, =CHCH$_2$C*H*$_3$, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.69 (O=*C*CH$_2$CH$_2$), 130.24 (H*C*=*C*H), 130.06 (H*C*=*C*H), 130.00 (H*C*=*C*H), 129.76 (H*C*=*C*H), 128.07 (H*C*=*C*H), 127.94 (H*C*=*C*H), 61.14 (HO*C*H$_2$CH$_2$N), 60.69 (HO*C*H$_2$CH$_2$N), 52.29 (HOCH$_2$*C*H$_2$N), 50.58 (HOCH$_2$*C*H$_2$N), 33.64 (O=C*C*H$_2$CH$_2$), 31.93 (*C*H$_2$), 29.79 (*C*H$_2$), 29.74 (*C*H$_2$), 29.69 (*C*H$_2$), 29.56 (*C*H$_2$), 29.47 (*C*H$_2$), 29.45 (*C*H$_2$), 29.35 (*C*H$_2$), 29.26 (*C*H$_2$), 27.25 (*C*H$_2$), 25.65 (HC=CH*C*H$_2$CH=CH), 25.36 (*C*H$_2$), 22.71 (*C*H$_2$), 14.15 (*C*H$_3$), 14.11 (=CHCH$_2$*C*H$_3$).; *m/z* (ES$^+$) 392.1 [M+Na]$^+$ (C18:1), 390.1 [M+Na]$^+$ (C18:2).

N,N-bis(2-hydroxyethyl)linoleamide (SBA 4.22) (Synthesised from soybean oil)



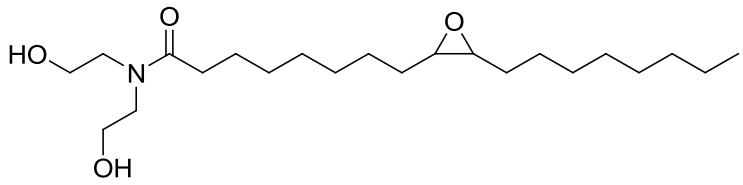
The general procedure for the synthesis of diethanolamine fatty amides was applied using hydrolysed soybean oil (30.0 g, 107 mmol, 1.0 equiv.), NMM (13.0 mL, 118

mmol, 1.1 equiv.) and ethyl chloroformate (11.3 mL, 118 mmol, 1.1 equiv.) followed by diethanolamine (11.3 g, 118 mmol, 1.1 equiv) and TEA (16.5 mL, 116 mmol, 1.1 equiv) to give the product as a yellow oil. (78 %); ν_{max}/cm^{-1} 3386 (O-H), 2922 (C-H), 2852 (C-H) 1617 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43 – 5.26 (m, 3H, *H*C=C*H*), 4.65 (s, 2H, O*H*), 3.77 (dt, *J* = 10.0, 5.1 Hz, 4H, HOC*H*$_2$CH$_2$N), 3.50 (dt, *J* = 10.3, 5.1 Hz, 4H, HOCH$_2$C*H*$_2$N), 2.83 – 2.71 (m, 1H, , HC=CHC*H*$_2$CH=CH), 2.38 (t, *J* = 7.9 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.15 – 1.89 (m, 4H, =CHC*H*$_2$CH$_2$), 1.69 – 1.51 (m, 2H, O=CC*H*$_2$CH$_2$), 1.35 – 1.24 (m, 17H, C*H*$_2$), 1.01 – 0.82 (m, 3H, =CHCH$_2$C*H*$_3$, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.60 (O=*C*CH$_2$CH$_2$), 130.21 (H*C*=*C*H), 130.04 (H*C*=*C*H), 129.99 (H*C*=*C*H), 129.74 (H*C*=*C*H), 128.28 (H*C*=*C*H), 128.24 (H*C*=*C*H), 128.04 (H*C*=*C*H), 127.91 (H*C*=*C*H), 127.72 (H*C*=*C*H), 61.08 (HO*C*H$_2$CH$_2$N), 60.64 (HO*C*H$_2$CH$_2$N), 52.25 (HOCH$_2$*C*H$_2$N), 50.54 (HOCH$_2$*C*H$_2$N), 33.62 (O=C*C*H$_2$CH$_2$), 31.92 (*C*H$_2$), 31.53 (*C*H$_2$), 29.77 (*C*H$_2$), 29.72 (*C*H$_2$), 29.67 (*C*H$_2$), 29.54 (*C*H$_2$), 29.44 (*C*H$_2$), 29.35 (*C*H$_2$), 29.24 (*C*H$_2$), 27.23 (*C*H$_2$), 25.63 (HC=CH*C*H$_2$CH=CH), 25.34 (*C*H$_2$), 22.70 (*C*H$_2$), 22.59 (*C*H$_2$), 14.14 (*C*H$_3$), 14.10 (=CHCH$_2$*C*H$_3$).; *m/z* (ES 392.1 $[M+Na]^+$ (C18:1), 390.1 $[M+Na]^+$ (C18:2).

6.4.13 General Procedure for the synthesis of epoxidised diethanolamine fatty amides

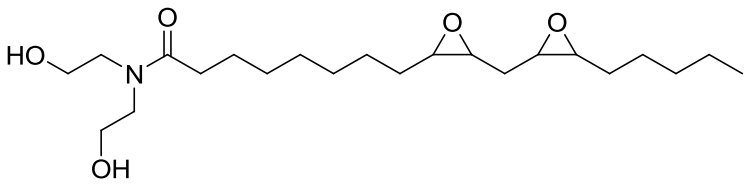
The desired diethanolamine fatty amide (1.0 equiv.) was dissolved in DCM (0.15 M) at room temperature. Peracetic acid (1 equiv. for oleic acid, 1.8 equiv. for linoleic acid and soybean oil, 1.4 equiv. for rapeseed oil) was added and left to react for 16 h. The reaction was washed with water (2 x 200 mL) then 15 % NaCl (100 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give pure product.

N,N-bis(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide



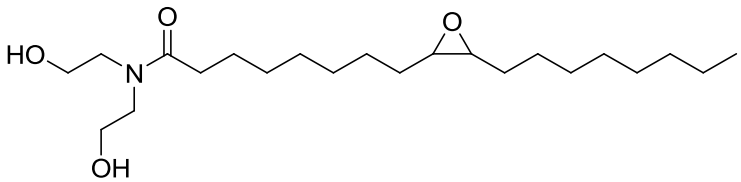
The general procedure for the synthesis of epoxidised diethanolamine fatty amides was applied using **OA 4.22** (25.0 g, 68 mmol, 1.0 equiv.) and peracetic acid (14.2 mL, 68 mmol, 1.0 equiv) to give the product as a pale yellow oil. (89 %); ν_{max}/cm^{-1} 3385 (O-H), 2922 (C-H), 2853 (C-H) 1616 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (br s, 2H, O*H*), 3.77 (dt, *J* = 10.9, 4.9 Hz, 4H, HOC*H*$_2$CH$_2$N), 3.51 (dt, *J* = 12.3, 6.9 Hz, 4H, HOCH$_2$C*H*$_2$N), 3.15 – 2.84 (m, 2H, CH$_2$C*H*(O)C*H*CH$_2$), 2.39 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.68 – 1.56 (m, 2H, O=CCH$_2$C*H*$_2$), 1.56 – 1.43 (m, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$CH$_2$), 1.43 – 1.23 (m, 18H, C*H*$_2$), 0.88 (t, *J* = 6.3 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.49 (O=*C*CH$_2$CH$_2$), 61.03 (HO*C*H$_2$CH$_2$N), 60.54 (HO*C*H$_2$CH$_2$N), 57.36 (CH$_2$*C*H(O)*C*HCH$_2$), 57.34 (CH$_2$*C*H(O)*C*HCH$_2$), 52.14 (HOCH$_2$*C*H$_2$N), 50.41 (HOCH$_2$*C*H$_2$N), 33.48 (O=C*C*H$_2$CH$_2$), 31.82 (*C*H$_2$), 29.50 (*C*H$_2$), 29.34 (*C*H$_2$), 29.26 (*C*H$_2$), 29.19 (*C*H$_2$), 27.76 (*C*H$_2$), 27.72 (*C*H$_2$), 26.55 (*C*H$_2$), 25.22 (O=CCH$_2$*C*H$_2$), 22.63 (*C*H$_2$), 14.09 (*C*H$_3$).; *m/z* (ES^+) 408.3 $[M+Na]^+$ (C18:1).

N,N-bis(2-hydroxyethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide



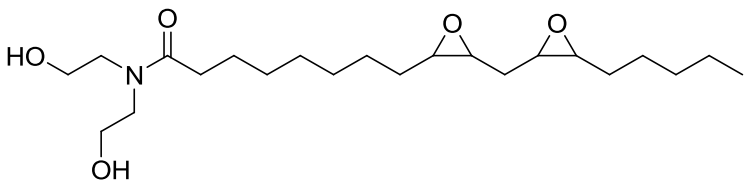
The general procedure for the synthesis of epoxidised diethanolamine fatty amides was applied using **LA 4.22** (25.0 g, 68 mmol, 1.0 equiv.) and peracetic acid (24.3 mL, 116 mmol, 1.7 equiv) to give the product as a pale yellow oil. (94 %); ν_{max}/cm^{-1} 3392 (O-H), 2922 (C-H), 2853 (C-H) 1615 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (br s, 2H, O*H*), 3.80 – 3.69 (m, 4H, HOC*H*$_2$CH$_2$N), 3.56 – 3.45 (m, 4H, HOCH$_2$C*H*$_2$N), 3.18 – 2.88 (m, 3H, CH$_2$C*H*(O)C*H*CH$_2$), 2.39 (t, *J* = 7.8 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.81 – 1.69 (m, 1H, (O)CHC*H*$_2$CH(O)), 1.68 – 1.57 (m, 2H, O=CCH$_2$C*H*$_2$), 1.55 – 1.45 (m, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$C*H*$_2$), 1.45 – 1.23 (m, 15H, C*H*$_2$), 0.89 (dt, *J* = 13.8, 7.0 Hz, 3H, (O)CHCH$_2$C*H*$_3$, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.32 (O=*C*CH$_2$CH$_2$), 60.86 (HO*C*H$_2$CH$_2$N), 60.39 (HO*C*H$_2$CH$_2$N), 57.26 (CH$_2$*C*H(O)*C*HCH$_2$), 57.24, 57.00 (CH$_2$*C*H(O)*C*HCH$_2$), 56.96 (CH$_2$*C*H(O)*C*HCH$_2$), 56.69 (CH$_2$*C*H(O)*C*HCH$_2$), 56.66 (CH$_2$*C*H(O)*C*HCH$_2$), 54.29 (CH$_2$*C*H(O)*C*HCH$_2$), 54.20 (CH$_2$*C*H(O)*C*HCH$_2$), 52.00 (HOCH$_2$*C*H$_2$N), 50.26 (HOCH$_2$*C*H$_2$N), 33.34 (O=C*C*H$_2$CH$_2$), 31.72 (*C*H$_2$), 31.52 (*C*H$_2$), 29.57 (*C*H$_2$), 29.40 (*C*H$_2$), 29.24 (*C*H$_2$), 29.19 (*C*H$_2$), 29.16 (*C*H$_2$), 29.08 (*C*H$_2$), 27.72 (*C*H$_2$), 27.71 (*C*H$_2$), 27.65 (*C*H$_2$), 26.99, 26.74 (*C*H$_2$), 26.45 (*C*H$_2$), 26.32 (*C*H$_2$), 26.10 (*C*H$_2$), 25.99 (*C*H$_2$), 25.11 (O=CCH$_2$*C*H$_2$), 22.53 (*C*H$_2$), 22.43 (*C*H$_2$), 14.00 ((O)CHCH$_2$*C*H$_3$), 13.88 (*C*H$_3$).; *m/z* (ES^+) 422.3 $[M+Na]^+$ (C18:2), 408.3 $[M+Na]^+$ (C18:1).

N,N-bis(2-hydroxyethyl)-8-(3-octyloxiran-2-yl)octanamide (Synthesised from rapeseed oil)



The general procedure for the synthesis of epoxidised diethanolamine fatty amides was applied using **RSA 4.22** (25.0 g, 68 mmol, 1.0 equiv.) and peracetic acid (16.3 mL, 95 mmol, 1.4 equiv) to give the product as a pale yellow oil. (94 %); ν_{max}/cm^{-1} 3386 (O-H), 2922 (C-H), 2853 (C-H) 1616 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dt, *J* = 10.2, 4.9 Hz, 4H, HOC*H*$_2$CH$_2$N), 3.52 (dt, *J* = 18.8, 5.0 Hz, 4H, HOCH$_2$C*H*$_2$N), 3.23 – 2.85 (m, 3H, CH$_2$C*H*(O)C*H*CH$_2$), 2.39 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.89 – 1.69 (m, 1H), 1.69 – 1.57 (m, 2H, O=CCH$_2$C*H*$_2$), 1.57 – 1.44 (m, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$C*H*$_2$), 1.42 – 1.18 (m, 17H, (O)CHCH$_2$C*H*$_3$, C*H*$_2$), 0.88 (t, *J* = 6.6 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.70 (O=*C*CH$_2$CH$_2$), 61.58 (HO*C*H$_2$CH$_2$N), 60.85 (HO*C*H$_2$CH$_2$N), 57.43 (CH$_2$*C*H(O)*C*HCH$_2$), 57.20 (CH$_2$*C*H(O)*C*HCH$_2$), 57.16 (CH$_2$*C*H(O)*C*HCH$_2$), 56.87 (CH$_2$*C*H(O)*C*HCH$_2$), 54.52 (CH$_2$*C*H(O)*C*HCH$_2$), 54.49 (CH$_2$*C*H(O)*C*HCH$_2$), 54.37 (CH$_2$*C*H(O)*C*HCH$_2$), 54.18 (CH$_2$*C*H(O)*C*HCH$_2$), 52.32 (HOCH$_2$*C*H$_2$N), 50.62 (HOCH$_2$*C*H$_2$N), 33.62 (O=C*C*H$_2$CH$_2$), 31.94 (*C*H$_2$), 29.79 (*C*H$_2$), 29.62 (*C*H$_2$), 29.42 (*C*H$_2$), 29.35 (*C*H$_2$), 29.31 (*C*H$_2$), 27.95 (*C*H$_2$), 27.90 (*C*H$_2$), 27.85 (*C*H$_2$), 26.68 (*C*H$_2$), 25.29 (O=CCH$_2$*C*H$_2$), 22.75 (*C*H$_2$), 14.19 ((O)CHCH$_2$*C*H$_3$), 14.08 (*C*H$_3$).; *m/z* (ES^+) 422.3 $[M+Na]^+$ (C18:2), 408.3 $[M+Na]^+$ (C18:1).

N,N-bis(2-hydroxyethyl)-8-(3-((3-pentyloxiran-2-yl)methyl)oxiran-2-yl)octanamide (Synthesised from soybean oil)



The general procedure for the synthesis of epoxidised diethanolamine fatty amides was applied using **SBA 4.22** (25.0 g, 68 mmol, 1.0 equiv.) and peracetic acid (21.2

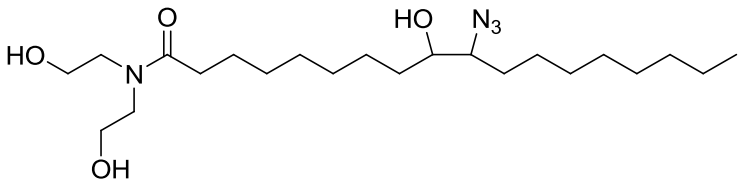
mL, 123 mmol, 1.8 equiv) to give the product as a pale yellow oil. (86 %); ν_{max}/cm^{-1} 3385 (O-H), 2922 (C-H), 2852 (C-H) 1616 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (br s, 2H, O*H*), 3.77 (dt, *J* = 10.6, 5.0 Hz, 4H, HOC*H*$_2$CH$_2$N), 3.51 (dt, *J* = 10.4, 5.0 Hz, 4H, HOCH$_2$C*H*$_2$N), 3.23 – 2.80 (m, 3H, CH$_2$C*H*(O)C*H*CH$_2$), 2.39 (t, *J* = 7.5 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.80 – 1.69 (m, 1H, (O)CHC*H*$_2$CH(O)), 1.67 – 1.58 (m, 2H, O=CCH$_2$C*H*$_2$), 1.57 – 1.42 (m, 6H, C*H*$_2$CH(O)CHC*H*$_2$, O=CCH$_2$CH$_2$C*H*$_2$), 1.41 – 1.17 (m, 15H, C*H*$_2$), 0.89 (dt, *J* = 9.8, 6.7 Hz, 1H, (O)CHCH$_2$C*H*$_3$, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.44 (O=*C*CH$_2$CH$_2$), 61.15 (HO*C*H$_2$CH$_2$N), 60.60 (HO*C*H$_2$CH$_2$N), 57.34 (CH$_2$*C*H(O)*C*HCH$_2$), 57.32 (CH$_2$*C*H(O)*C*HCH$_2$), 57.09 (CH$_2$*C*H(O)*C*HCH$_2$), 57.06 (CH$_2$*C*H(O)*C*HCH$_2$), 56.79 (CH$_2$*C*H(O)*C*HCH$_2$), 56.75 (CH$_2$*C*H(O)*C*HCH$_2$), 54.41 (CH$_2$*C*H(O)*C*HCH$_2$), 54.38 (CH$_2$*C*H(O)*C*HCH$_2$), 54.28 (CH$_2$*C*H(O)*C*HCH$_2$), 52.14 (HOCH$_2$*C*H$_2$N), 50.45 (HOCH$_2$*C*H$_2$N), 33.48 (O=C*C*H$_2$CH$_2$), 31.90 (*C*H$_2$), 31.82 (*C*H$_2$), 31.63 (*C*H$_2$), 29.67 (*C*H$_2$), 29.63 (*C*H$_2$), 29.50 (*C*H$_2$), 29.34 (*C*H$_2$), 29.30 (*C*H$_2$), 29.19 (*C*H$_2$), 27.83 (*C*H$_2$), 27.77 (*C*H$_2$), 27.13 (*C*H$_2$), 26.87 (*C*H$_2$), 26.56 (*C*H$_2$), 26.53 (*C*H$_2$), 26.43 (*C*H$_2$), 26.21 (*C*H$_2$), 26.10 (*C*H$_2$), 25.21 (O=CCH$_2$*C*H$_2$), 22.63 (*C*H$_2$), 22.54 (*C*H$_2$), 14.09 ((O)CHCH$_2$*C*H$_3$), 13.97 (*C*H$_3$).; *m/z* (ES^+) 422.3 $[M+Na]^+$ (C18:2), 408.3 $[M+Na]^+$ (C18:1).

6.4.14 General Procedure for the synthesis of azido diethanolamine fatty amides

The desired epoxidised fatty amide (1 equiv.) was dissolved in ethanol:water (0.0.8 M, 5:1) at 100 °C. Sodium azide (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) and ammonium chloride (2 equiv. for oleic acid, 3 equiv. for linoleic acid, rapeseed oil and soybean oil) were added and left to react overnight at 100 °C. The reaction mixture was diluted with water (200 mL) and extracted with chloroform. The organic layer was washed with 15 % NaCl and dried

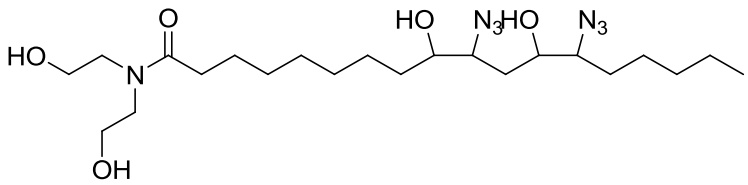
over $MgSO_4$. The solvent was removed *in vacuo* to produce pure product without further purification.

10-Azido-9-hydroxy-N,N-bis(2-hydroxyethyl)octadecanamide (AzOA 4.23)



The general procedure for the synthesis of azido diethanolamine fatty amides was applied using **epoxy OA 4.22** (20.0 g, 52 mmol, 1.0 equiv.), NaN_3 (6.7 g, 104 mmol, 2 equiv.) and NH_4Cl (5.6 g, 104 mmol, 2.0 equiv) to give the product as a pale yellow oil. (82 %); ν_{max}/cm^{-1} 3338 (O-H), 2923 (C-H), 2853 (C-H), 2098 ($N=N^+=N^-$), 1616 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 4.51 (br s, 2H, O*H*), 3.78 (dt, *J* = 9.8, 4.6 Hz, 4H, HOCH_2CH_2N), 3.63 – 3.37 (m, 5H, HOCH_2CH_2N, CH_2C*H*(OH)), 3.24 – 3.08 (m, 1H, (N_3)C*H*CH_2), 2.40 (t, *J* = 7.3 Hz, 2H, O=CCH_2CH_2), 1.69 – 1.57 (m, 4H, O=CCH_2CH_2, (N_3)CHCH_2), 1.57 – 1.43 (m, 4H, CH_2CH(OH), CH_2), 1.42 – 1.18 (m, 18H, CH_2), 0.88 (t, *J* = 6.4 Hz, 3H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.72 (O=*C*CH_2CH_2), 73.60 (CH_2*C*H(OH)), 73.53 (CH_2*C*H(OH)), 67.21 ((N_3)*C*HCH_2), 66.96 ((N_3)*C*HCH_2), 61.16 (HO*C*H_2CH_2N), 61.12 (HO*C*H_2CH_2N), 60.62 (HO*C*H_2CH_2N), 52.20 (HOCH_2*C*H_2N), 50.43 (HOCH_2*C*H_2N), 50.37 (HOCH_2*C*H_2N), 34.23 (*C*H_2CH(OH)), 34.15 (*C*H_2CH(OH)), 33.48 (O=C*C*H_2CH_2), 31.90 (*C*H_2), 31.88 (*C*H_2), 30.84 (*C*H_2), 30.69 (*C*H_2), 29.74 (*C*H_2), 29.66 (*C*H_2), 29.58 (*C*H_2), 29.52 (*C*H_2), 29.30 (*C*H_2), 29.26 (*C*H_2), 29.20 (*C*H_2), 29.15 (*C*H_2), 29.10 (*C*H_2), 26.37 (*C*H_2), 26.21 (*C*H_2), 25.78 (*C*H_2), 25.52 (*C*H_2), 25.20 (*C*H_2), 22.69 (*C*H_2), 14.15 (*C*H_3).; *m/z* (ES^+) 451.2 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxy-N,N-bis(2-hydroxyethyl)octadecanamide (AzLA 4.23)

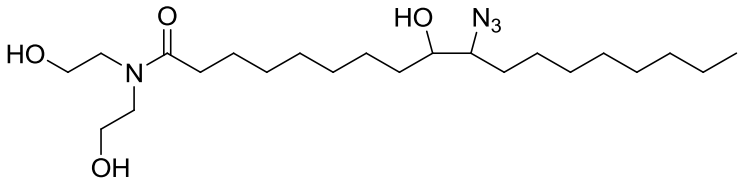


The general procedure for the synthesis of azido diethanolamine fatty amides was applied using **epoxy LA 4.22** (20.0 g, 52 mmol, 1.0 equiv.), NaN_3 (9.8 g, 156 mmol, 3 equiv.) and NH_4Cl (8.0 g, 156 mmol, 3.0 equiv) to give the product as a pale yellow oil. (82 %); ν_{max}/cm^{-1} 3329 (O-H), 2924 (C-H), 2854 (C-H), 2098 ($N=N^+=N^-$), 1615 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (br s, 2H, O*H*), 3.94 – 3.72 (m, 5H, HOC*H*$_2$CH$_2$N, CH$_2$C*H*(OH)), 3.64 – 3.34 (m, 5H, HOCH$_2$C*H*$_2$N, CH$_2$C*H*(OH), (N_3)C*H*CH$_2$), 3.24 – 3.07 (m, 1H, (N_3)C*H*CH$_2$), 2.40 (t, *J* = 6.1 Hz, 2H, O=CC*H*$_2$CH$_2$), 1.73 – 1.55 (m, 5H, O=CCH$_2$C*H*$_2$, (N_3)CHC*H*$_2$), 1.55 – 1.24 (m, 20H, C*H*$_2$CH(OH), C*H*$_2$), 0.89 (dt, *J* = 6.7 Hz, 3H, (N_3)CHCH$_2$C*H*$_3$, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.80 (O=*C*CH$_2$CH$_2$), 74.34 (CH$_2$*C*H(OH)), 74.22 (CH$_2$*C*H(OH)), 73.60 (CH$_2$*C*H(OH)), 73.54 (CH$_2$*C*H(OH)), 73.15 (CH$_2$*C*H(OH)), 72.92 (CH$_2$*C*H(OH)), 70.58 (CH$_2$*C*H(OH)), 70.51 (CH$_2$*C*H(OH)), 70.25 (CH$_2$*C*H(OH)), 69.72 (CH$_2$*C*H(OH)), 67.50 ((N_3)*C*HCH$_2$), 67.40 ((N_3)*C*HCH$_2$), 67.19 ((N_3)*C*HCH$_2$), 66.93 ((N_3)*C*HCH$_2$), 66.66 ((N_3)*C*HCH$_2$), 66.47 ((N_3)*C*HCH$_2$), 63.61 ((N_3)*C*HCH$_2$), 60.91 (HO*C*H$_2$CH$_2$N), 60.48 (HO*C*H$_2$CH$_2$N), 52.11 (HOCH$_2$*C*H$_2$N), 50.31 (HOCH$_2$*C*H$_2$N), 34.21 (*C*H$_2$CH(OH)), 34.13 (*C*H$_2$CH(OH)), 33.37 (O=C*C*H$_2$CH$_2$), 31.87 (*C*H$_2$), 31.79 (*C*H$_2$), 31.64 (*C*H$_2$), 30.83 (*C*H$_2$), 30.70 (*C*H$_2$), 30.47 (*C*H$_2$), 29.73 (*C*H$_2$), 29.65 (*C*H$_2$), 29.51 (*C*H$_2$), 29.25 (*C*H$_2$), 29.19 (*C*H$_2$), 29.03 (*C*H$_2$), 26.35 (*C*H$_2$), 26.20 (*C*H$_2$), 25.99 (*C*H$_2$), 25.77 (*C*H$_2$), 25.52 (*C*H$_2$), 25.20 (*C*H$_2$), 25.09 (*C*H$_2$), 22.69 (*C*H$_2$), 22.62 (*C*H$_2$), 22.56 (*C*H$_2$), 14.15

((N_3)CHCH_2CH_3), 14.09 (CH_3), 14.05 (CH_3).; *m/z* (ES^+) 508.2 $[M+Na]^+$ (C18:2), 451.2 $[M+Na]^+$ (C18:1).

10-Azido-9-hydroxy-N,N-bis(2-hydroxyethyl)octadecanamide (AzRSA 4.23)

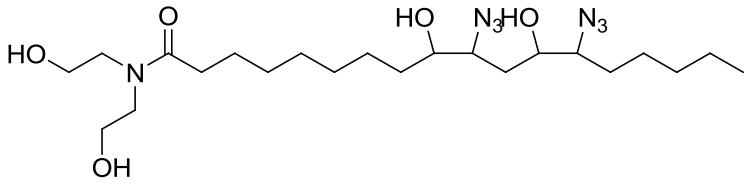
(Synthesised from rapeseed oil)



The general procedure for the synthesis of azido diethanolamine fatty amides was applied using **epoxy SBA 4.22** (15.0 g, 38 mmol, 1.0 equiv.), NaN_3 (7.4 g, 114 mmol, 3 equiv.) and NH_4Cl (6.1 g, 114 mmol, 3.0 equiv) to give the product as a pale yellow oil. (62 %); ν_{max}/cm^{-1} 3359 (O-H), 2923 (C-H), 2853 (C-H), 2098 ($N=N^+=N^-$), 1617 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.61 (br s, 2H, O*H*), 3.82 – 3.71 (m, 4H, HOC*H*$_2$CH_2N), 3.58 – 3.44 (m, 5H, HOCH_2C*H*$_2$N, CH_2C*H*(OH)), 3.23 – 3.09 (m, 1H, (N_3)C*H*CH_2), 2.39 (t, *J* = 7.3 Hz, 2H, O=CC*H*$_2$CH_2), 1.71 – 1.57 (m, 4H, (N_3)CHC*H*$_2$, O=CCH_2C*H*$_2$), 1.55 – 1.40 (m, 4H, C*H*$_2$CH(OH), C*H*$_2$), 1.40 – 1.21 (m, 18H, C*H*$_2$), 0.88 (t, *J* = 6.5 Hz, 3H, C*H*$_3$).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.59 (O=*C*CH_2CH_2), 73.53 (CH_2*C*H(OH)), 73.47 (CH_2*C*H(OH)), 67.10 ((N_3)*C*HCH_2), 66.86 ((N_3)*C*HCH_2), 60.96 (HO*C*H_2CH_2N), 60.92 (HO*C*H_2CH_2N), 60.51 (HO*C*H_2CH_2N), 52.11 (HOCH_2*C*H_2N), 50.37 (HOCH_2*C*H_2N), 50.31 (HOCH_2*C*H_2N), 34.12 (*C*H_2CH(OH)), 34.05 (*C*H_2CH(OH)), 33.40 (O=C*C*H_2CH_2), 31.81 (*C*H_2), 30.74 (*C*H_2), 30.61 (*C*H_2), 29.67 (*C*H_2), 29.59 (*C*H_2), 29.51 (*C*H_2), 29.45 (*C*H_2), 29.24 (*C*H_2), 29.20 (*C*H_2), 29.14 (*C*H_2), 29.05 (*C*H_2), 26.30 (*C*H_2), 26.16 (*C*H_2), 25.93 (*C*H_2), 25.71 (*C*H_2), 25.46 (*C*H_2), 25.34 (*C*H_2), 25.14 (*C*H_2),

22.63 (CH_2), 14.09 (CH_3), 13.99 (CH_3).; *m/z* (ES^+) 508.2 $[M+Na]^+$ (C18:2), 451.2 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxy-N,N-bis(2-hydroxyethyl)octadecanamide (AzSBA 4.23) (Synthesised from soybean oil)



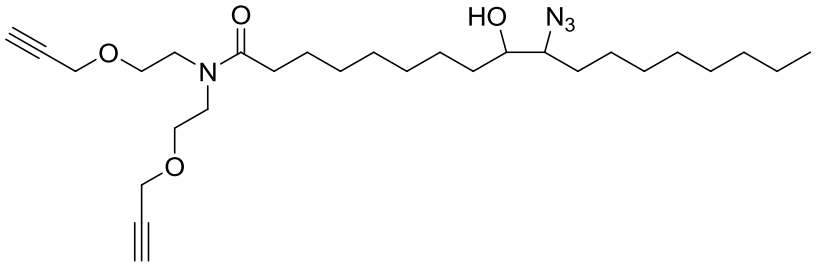
The general procedure for the synthesis of azido diethanolamine fatty amides was applied using **epoxy OA 4.22** (15.0 g, 38 mmol, 1.0 equiv.), NaN_3 (7.4 g, 114 mmol, 3 equiv.) and NH_4Cl (6.1 g, 114 mmol, 3.0 equiv) to give the product as a pale yellow oil. (85 %); ν_{max}/cm^{-1} 3358 (O-H), 2923 (C-H), 2853 (C-H), 2099 ($N=N^+=N^-$), 1615 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (br s, 2H, O*H*), 3.96 – 3.84 (m, 1H, CH_2CH(OH)), 3.76 (dd, *J* = 11.3, 6.1 Hz, 4H, $HOCH_2CH_2N$), 3.51 (dd, *J* = 11.7, 5.1 Hz, 5H, $HOCH_2CH_2N$, CH_2CH(OH), $(N_3)CHCH_2$), 3.23 – 3.07 (m, 1H, $(N_3)CHCH_2$), 2.39 (t, *J* = 6.6 Hz, 2H, $O=CCH_2CH_2$), 1.78 – 1.54 (m, 5H, $O=CCH_2CH_2$, $(N_3)CHCH_2$), 1.54 – 1.24 (m, 20H, CH_2CH(OH), CH_2), 0.89 (dt, *J* = 6.8 Hz, 3H, $(N3)CHCH_2CH_3$, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.65 ($O=CCH_2CH_2$), 74.29 (CH_2CH(OH)), 74.18 (CH_2CH(OH)), 73.55 (CH_2CH(OH)), 73.51 (CH_2CH(OH)), 73.09 (CH_2CH(OH)), 72.86 (CH_2CH(OH)), 70.47 (CH_2CH(OH)), 70.27 (CH_2CH(OH)), 70.18 (CH_2CH(OH)), 69.72 (CH_2CH(OH)), 67.52 ($(N_3)CHCH_2$), 67.46 ($(N_3)CHCH_2$), 67.36 ($(N_3)CHCH_2$), 67.14 ($(N_3)CHCH_2$), 66.89 ($(N_3)CHCH_2$), 66.60 ($(N_3)CHCH_2$), 66.47 ($(N_3)CHCH_2$), 66.41 ($(N_3)CHCH_2$), 63.55 ($(N_3)CHCH_2$), 61.00 ($HOCH_2CH_2N$), 60.84 ($HOCH_2CH_2N$), 60.61 ($HOCH_2CH_2N$), 60.45 ($HOCH_2CH_2N$), 52.08 ($HOCH_2CH_2N$), 50.44

(HOCH$_2$*C*H$_2$N), 50.30 (HOCH$_2$*C*H$_2$N), 34.15 (*C*H$_2$CH(OH)), 33.60 (*C*H$_2$CH(OH)), 33.41 (*C*H$_2$CH(OH)), 33.33 (O=C*C*H$_2$CH$_2$), 31.91 (*C*H$_2$), 31.85 (*C*H$_2$), 31.76 (*C*H$_2$), 31.61 (*C*H$_2$), 30.78 (*C*H$_2$), 30.65 (*C*H$_2$), 30.43 (*C*H$_2$), 30.22 (*C*H$_2$), 29.69 (*C*H$_2$), 29.47 (*C*H$_2$), 29.35 (*C*H$_2$), 29.26 (*C*H$_2$), 29.22 (*C*H$_2$), 29.15 (*C*H$_2$), 29.01 (*C*H$_2$), 26.32 (*C*H$_2$), 26.18 (*C*H$_2$), 25.96 (*C*H$_2$), 25.73 (*C*H$_2$), 25.48 (*C*H$_2$), 25.36 (*C*H$_2$), 25.16 (*C*H$_2$), 25.06 (*C*H$_2$), 22.65 (*C*H$_2$), 22.58 (*C*H$_2$), 22.52 (*C*H$_2$), 14.11 ((N$_3$)CHCH$_2$*C*H$_3$), 14.05 (*C*H$_3$), 14.01 (*C*H$_3$).; *m/z* (ES$^+$) 508.2 [M+Na]$^+$ (C18:2), 451.2 [M+Na]$^+$ (C18:1).

6.4.15 General Procedure for the synthesis of propargyl azido diethanolamine fatty amides

The desired azido diethanolamine fatty amide (1.0 equiv.) was dissolved in dry THF (0.5 M) at -78 °C. NaH (95 %) (2.2 equiv.) was added and left to react for 30 mins. Propargyl bromide (80 wt. % in toluene) (2.2 equiv.) was added dropwise and the reaction mixture was left to warm to room temperature overnight. The reaction mixture was quenched with aqueous acid (20 mL 2 M HCl) and extracted using Et$_2$O. The organic layer was washed with water (2 x 50 mL) then saturated NaCl (50 mL) and dried over MgSO$_4$. The solvent was removed *in vacuo* to give crude product which was purified through silica plug (8:1) (Et$_2$O:Hex) to give pure product.

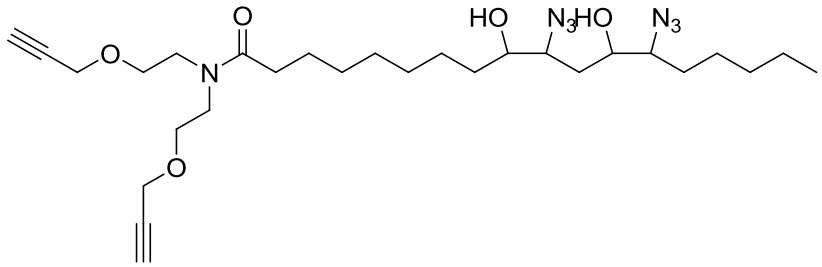
10-Azido-9-hydroxy-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadecanamide (DEtOA 4.11)



The general procedure for the synthesis of propargyl azido diethanolamine fatty amides was applied using **AzOA 4.23** (15.0 g, 35 mmol, 1.0 equiv.), NaH (1.9 g, 77 mmol, 2.2 equiv) and propargyl bromide (8.6 mL, 77 mmol, 2.2 equiv.) to give the product as a pale yellow oil. (52 %); ν_{max}/cm^{-1} 3350 (O-H), 3305 (≡C-H), 2924 (C-H), 2854 (C-H), 2100 ($N=N^{+}=N^{-}$), 1626 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (dd, *J* = 9.4, 2.1 Hz, 4H, HC≡CC*H*$_2$O), 3.70 – 3.63 (m, 4H, OC*H*$_2$CH$_2$N), 3.59 (dt, *J* = 10.5, 5.2 Hz, 4H, HOCH$_2$C*H*$_2$N), 3.56 – 3.51 (m, 1H, CH$_2$C*H*(OH)), 3.17 (m, 1H, (N_3)C*H*CH$_2$), 2.46 (dt, *J* = 4.1, 2.3 Hz, 2H, *H*C≡CCH$_2$O), 2.40 – 2.34 (m, 2H, O=CCH$_2$CH$_2$), 1.62 (dd, *J* = 14.1, 7.1 Hz, 4H, O=CC*H*$_2$CH$_2$, (N_3)CHC*H*$_2$), 1.48 (dt, *J* = 16.7, 9.2 Hz, 4H, C*H*$_2$CH(OH), C*H*$_2$), 1.30 (d, *J* = 18.4 Hz, 18H, C*H*$_2$), 0.88 (t, *J* = 6.4 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.84 (O=*C*CH$_2$CH$_2$), 79.57 (H*C*≡CCH$_2$O), 79.24 (H*C*≡CCH$_2$O), 74.83 (HC≡*C*CH$_2$O), 74.46 (HC≡*C*CH$_2$O), 73.41 (CH$_2$*C*H(OH)), 73.38 (CH$_2$*C*H(OH)), 68.57 (HO*C*H$_2$CH$_2$N), 67.88 ((N_3)*C*HCH$_2$), 67.82 ((N_3)*C*HCH$_2$), 67.02 ((N_3)*C*HCH$_2$), 66.94 ((N_3)*C*HCH$_2$), 58.40 (HC≡C*C*H$_2$O), 58.17 (HC≡C*C*H$_2$O), 48.74 (HOCH$_2$*C*H$_2$N), 46.33 (HOCH$_2$*C*H$_2$N), 34.12 (*C*H$_2$CH(OH)), 34.08 (*C*H$_2$CH(OH)), 33.92 (O=C*C*H$_2$CH$_2$), 32.92 (*C*H$_2$), 31.79 (*C*H$_2$), 31.76 (*C*H$_2$), 30.67 (*C*H$_2$), 30.63 (*C*H$_2$), 29.61 (*C*H$_2$), 29.54 (*C*H$_2$), 29.46 (*C*H$_2$), 29.41 (*C*H$_2$), 29.39 (*C*H$_2$), 29.30 (*C*H$_2$), 29.25 (*C*H$_2$), 29.19 (*C*H$_2$),

29.15 (CH_2), 28.98 (CH_2), 26.25 (CH_2), 26.17 (CH_2), 25.63 (CH_2), 25.51 (CH_2), 25.13 (CH_2), 15.16 (CH_2), 14.04 (CH_3).; *m/z* (ES^+) 527.2 $[M+Na]^+$ (C18:1).

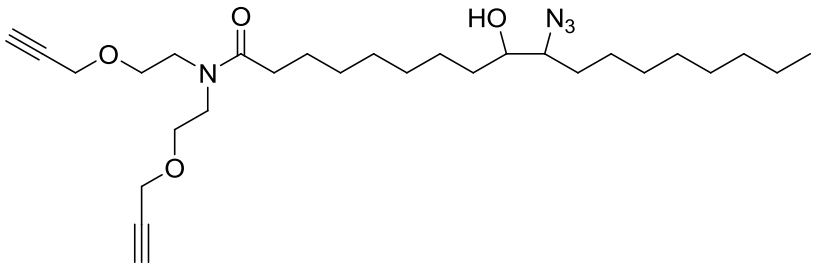
10,13-Diazido-9,12-dihydroxy-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadecanamide (DEtLA 4.11)



The general procedure for the synthesis of propargyl azido diethanolamine fatty amides was applied using **AzLA 4.23** (15.0 g, 31 mmol, 1.0 equiv.), NaH (1.6 g, 68 mmol, 2.2 equiv) and propargyl bromide (7.6 mL, 68 mmol, 2.2 equiv.) to give the product as a pale yellow oil. (31 %); ν_{max}/cm^{-1} 3350 (O-H), 3304 (≡C-H), 2924 (C-H), 2854 (C-H), 2100 ($N=N^+=N^-$), 1621 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 4.14 (dd, *J* = 9.3, 1.9 Hz, 4H, HC≡CCH_2O), 3.99 – 3.72 (m, 1H, CH_2CH(OH), (N_3)C*H*CH_2), 3.71 – 3.63 (m, 4H, OCH_2CH_2N), 3.63 – 3.56 (m, 4H, OCH_2CH_2N), 3.56 – 3.52 (m, 1H, CH_2CH(OH)), 3.28 – 3.09 (m, 1H, (N_3)C*H*CH_2), 2.45 (dt, *J* = 5.1, 2.8 Hz, 2H, *H*C≡CCH_2O), 2.38 (t, *J* = 8.5 Hz, 2H, O=CCH_2CH_2), 1.72 – 1.54 (m, 5H, O=CCH_2CH_2, (N_3)CHCH_2), 1.53 – 1.23 (m, 20H, CH_2CH(OH), CH_2), 0.96 – 0.78 (m, 3H, (N_3)$CHCH_2CH_3$, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.10 (O=*C*CH_2CH_2), 79.69 (H*C*≡CCH_2O), 79.35 (H*C*≡CCH_2O), 74.93 (HC≡*C*CH_2O), 74.56 (HC≡*C*CH_2O), 73.57 (CH_2CH(OH)), 73.15 (CH_2CH(OH)), 72.82 (CH_2CH(OH)), 70.52 (CH_2CH(OH)), 70.43 (CH_2CH(OH)), 70.35 (CH_2CH(OH)), 70.07 (CH_2CH(OH)), 68.71 (HO*C*H_2CH_2N), 68.00 (HO*C*H_2CH_2N), 67.47 ((N_3)*C*HCH_2), 67.25 ((N_3)*C*HCH_2), 67.15 ((N_3)*C*HCH_2), 66.97 ((N_3)*C*HCH_2), 66.83

($(N_3)CHCH_2$), 63.82 ($(N_3)CHCH_2$), 63.70 ($(N_3)CHCH_2$), 58.55 ($HC{\equiv}CCH_2O$), 58.33 ($HC{\equiv}CCH_2O$), 48.91 ($HOCH_2CH_2N$), 46.49 ($HOCH_2CH_2N$), 34.43 ($CH_2CH(OH)$), 34.32 ($CH_2CH(OH)$), 34.27 ($CH_2CH(OH)$), 33.97 ($CH_2CH(OH)$), 33.17 ($CH_2CH(OH)$), 33.08 ($O{=}CCH_2CH_2$), 31.98 (CH_2), 31.92 (CH_2), 31.79 (CH_2), 31.68 (CH_2), 30.91 (CH_2), 30.86 (CH_2), 30.78 (CH_2), 30.60 (CH_2), 30.55 (CH_2), 29.75 (CH_2), 29.66 (CH_2), 29.58 (CH_2), 29.51 (CH_2), 29.40 (CH_2), 29.35 (CH_2), 29.31 (CH_2), 29.18 (CH_2), 29.09 (CH_2), 26.34 (CH_2), 26.26 (CH_2), 26.00 (CH_2), 25.95 (CH_2), 25.73 (CH_2), 25.65 (CH_2), 25.60 (CH_2), 25.42 (CH_2), 25.27 (CH_2), 24.81 (CH_2), 24.75 (CH_2), 22.71 (CH_2), 22.63 (CH_2), 22.57 (CH_2), 14.17 ($(N_3)CHCH_2CH_3$), 14.05 (CH_3).; *m/z* (ES^+) 584.2 $[M+Na]^+$ (C18:2), 527.2 $[M+Na]^+$ (C18:1).

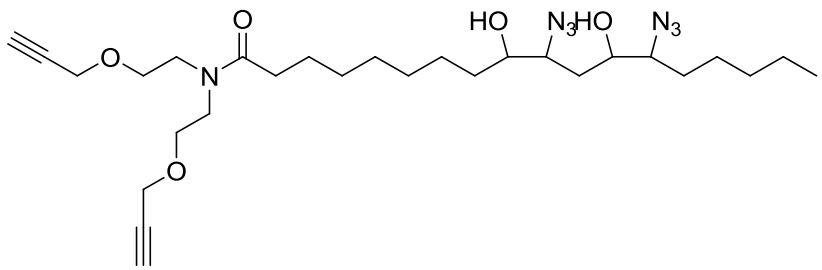
10-Azido-9-hydroxy-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadecanamide (DEtRSA 4.11) (Synthesised from rapeseed oil)



The general procedure for the synthesis of propargyl azido diethanolamine fatty amides was applied using **AzRSA 4.23** (11.0 g, 23 mmol, 1.0 equiv.), NaH (1.2 g, 50 mmol, 2.2 equiv) and propargyl bromide (5.6 mL, 50 mmol, 2.2 equiv.) to give the product as a pale yellow oil. (32 %);ν_{max}/cm^{-1} 3350 (O-H), 3307 (≡C-H), 2924 (C-H), 2854 (C-H), 2100 ($N{=}N^+{=}N^-$), 1625 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 4.14 (dd, *J* = 7.0, 2.3 Hz, 4H, $HC{\equiv}CCH_2O$), 3.71 – 3.63 (m, 4H, OCH_2CH_2N), 3.63 – 3.56 (m, 4H, OCH_2CH_2N), 3.56 – 3.52 (m, 1H, $CH_2CH(OH)$), 3.25 – 3.13 (m, 1H,

(N_3)C*H*CH_2), 2.45 (dt, *J* = 10.1, 2.2 Hz, 2H, *H*C≡CCH_2O), 2.38 (t, *J* = 7.3 Hz, 2H, O=CCH_2CH_2), 1.70 – 1.56 (m, 4H, O=CCH_2CH_2, (N_3)CHCH_2), 1.56 – 1.24 (m, 22H, CH_2CH(OH), CH_2), 0.88 (t, *J* = 6.3 Hz, 3H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.99 (O=*C*CH_2CH_2), 79.64 (H*C*≡CCH_2O), 79.31 (H*C*≡CCH_2O), 74.89 (HC≡*C*CH_2O), 74.53 (HC≡*C*CH_2O), 73.80 (CH_2*C*H(OH)), 73.52 (CH_2*C*H(OH)), 70.41 (CH_2*C*H(OH)), 70.27 (CH_2*C*H(OH)), 70.03 (CH_2*C*H(OH)), 68.68 (HO*C*H_2CH_2N), 67.96 (HO*C*H_2CH_2N), 67.38((N_3)*C*HCH_2), 67.17((N_3)*C*HCH_2), 67.08((N_3)*C*HCH_2), 66.75((N_3)*C*HCH_2), 63.61 ((N_3)*C*HCH_2), 58.50 (HC≡C*C*H_2O), 58.28 (HC≡C*C*H_2O), 48.85 (HOCH_2*C*H_2N), 46.43 (HOCH_2*C*H_2N), 34.25 (*C*H_2CH(OH)), 34.20 (*C*H_2CH(OH)), 33.03 (O=C*C*H_2CH_2), 31.94 (*C*H_2), 31.88 (*C*H_2), 30.83 (*C*H_2), 30.79 (*C*H_2), 29.71 (*C*H_2), 29.63 (*C*H_2), 29.55 (*C*H_2), 29.48 (*C*H_2), 29.38 (*C*H_2), 29.28 (*C*H_2), 29.02 (*C*H_2), 26.31 (*C*H_2), 26.24 (*C*H_2), 25.70 (*C*H_2), 25.61 (*C*H_2), 25.22 (*C*H_2), 24.81 (*C*H_2), 22.68 (*C*H_2), 14.14 (*C*H_3).; *m/z* (ES^+) 584.2 $[M+Na]^+$ (C18:2), 527.2 $[M+Na]^+$ (C18:1).

10,13-Diazido-9,12-dihydroxy-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadecanamide (DEtSBA 4.11) (Synthesised from soybean oil)



The general procedure for the synthesis of propargyl azido diethanolamine fatty amides was applied using **AzSBA 4.23** (15.0 g, 31 mmol, 1.0 equiv.), NaH (1.6 g, 68 mmol, 2.2 equiv) and propargyl bromide (7.6 mL, 68 mmol, 2.2 equiv.) to give the product as a pale yellow oil. (26 %);ν_{max}/cm^{-1} 3350 (O-H), 3306 (≡C-H), 2923 (C-H),

2853 (C-H), 2100 ($N=N^+=N^-$), 1621 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.14 (dd, *J* = 7.2, 2.3 Hz, 4H, HC≡CC*H*$_2$O), 3.99 – 3.73 (m, 1H, CH_2CH(OH), (N_3)C*H*CH_2), 3.71 – 3.63 (m, 4H, OC*H*$_2CH_2N$), 3.63 – 3.54 (m, 5H, OCH_2CH_2N, CH_2CH(OH)), 3.25 – 3.12 (m, 1H, (N_3)C*H*CH_2), 2.46 (dt, *J* = 7.0, 2.4 Hz, 2H, *H*C≡CCH_2O), 2.38 (t, *J* = 7.9 Hz, 2H, O=CC*H*$_2CH_2$), 1.71 – 1.56 (m, 5H, O=CCH_2CH_2, (N_3)CHC*H*$_2$), 1.56 – 1.24 (m, 20H, C*H*$_2$CH(OH), CH_2), 0.96 – 0.80 (m, 3H, (N_3)$CHCH_2CH_3$, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.22 (O=*C*CH_2CH_2), 79.61 (H*C*≡CCH_2O), 79.28 (H*C*≡CCH_2O), 74.91 (HC≡*C*CH_2O), 74.55 (HC≡*C*CH_2O), 74.37 (CH_2CH(OH)), 74.22 (CH_2CH(OH)), 73.77 (CH_2CH(OH)), 73.52 (CH_2CH(OH)), 73.04 (CH_2CH(OH)), 72.76 (CH_2CH(OH)), 70.47 (CH_2CH(OH)), 70.40 (CH_2CH(OH)), 70.23 (CH_2CH(OH)), 70.01 (CH_2CH(OH)), 68.62 (HO*C*H_2CH_2N), 67.90 (HO*C*H_2CH_2N), 67.65 ((N_3)*C*HCH_2), 67.57 ((N_3)*C*HCH_2), 67.35 ((N_3)*C*HCH_2), 67.18 ((N_3)*C*HCH_2), 67.13 ((N_3)*C*HCH_2), 67.04 ((N_3)*C*HCH_2), 66.81 ((N_3)*C*HCH_2), 66.69 ((N_3)*C*HCH_2), 63.69 ((N_3)*C*HCH_2), 63.60 ((N_3)*C*HCH_2), 58.48 (HC≡C*C*H_2O), 58.26 (HC≡C*C*H_2O), 48.87 ($HOCH_2CH_2N$), 46.44 ($HOCH_2CH_2N$), 35.43(*C*H_2CH(OH)), 35.06(*C*H_2CH(OH)), 34.98(*C*H_2CH(OH)),34.29(*C*H_2CH(OH)), 34.20(*C*H_2CH(OH)), 34.15(*C*H_2CH(OH)), 33.99(*C*H_2CH(OH)), 33.01, (O=C*C*H_2CH_2), 31.92 (*C*H_2), 31.86 (*C*H_2), 31.75 (*C*H_2), 31.62 (*C*H_2), 30.80 (*C*H_2), 30.76 (*C*H_2), 30.69 (*C*H_2), 30.45 (*C*H_2), 29.69 (*C*H_2), 29.56 (*C*H_2), 29.53 (*C*H_2), 29.48 (*C*H_2), 29.36 (*C*H_2), 29.30 (*C*H_2), 29.26 (*C*H_2), 29.23 (*C*H_2), 29.14 (*C*H_2), 28.99 (*C*H_2), 26.30 (*C*H_2), 26.22 (*C*H_2), 25.95 (*C*H_2), 25.68 (*C*H_2), 25.56 (*C*H_2), 25.48 (*C*H_2), 25.36 (*C*H_2), 25.21 (*C*H_2), 24.85 (*C*H_2), 24.76 (*C*H_2), 22.69 (*C*H_2), 22.66 (*C*H_2), 22.59 (*C*H_2), 22.52 (*C*H_2), 14.12 ((N_3)$CHCH_2CH_3$), 14.01 (*C*H_3).; *m/z* (ES^+) 584.2 $[M+Na]^+$ (C18:2), 527.2 $[M+Na]^+$ (C18:1).

6.4.16 General Procedure for the Polymerisation of the Monomers

The desired monomer was cast in a silicone mould and heated at 100 °C for 24 hours. After cooling the polymer was removed from the mould ready for testing. The polymers didn't dissolve in solvent therefore have only been characterised by IR.

POE (4.13): The general procedure for the polymerisation of the monomers was applied using **OE 4.7.** ν_{max}/cm^{-1} 3359 (O-H), 2923 (C-H), 2853 (C-H), 1735 (C=O), 1552 (C=C triazole), 1458 (N=N triazole).

PLE (4.13): The general procedure for the polymerisation of the monomers was applied using **LE 4.7**. ν_{max}/cm^{-1} 3352 (O-H), 2923 (C-H), 2854 (C-H), 2103 ($N=N^{+}=N^{-}$), 1735 (C=O), 1554 (C=C triazole), 1458 (N=N triazole).

PRSE (4.13) (Synthesised from rapeseed oil): The general procedure for the polymerisation of the monomers was applied using **RSE 4.7**. ν_{max}/cm^{-1} 3353 (O-H), 2922 (C-H), 2853 (C-H), 1736 (C=O), 1555 (C=C triazole), 1458 (N=N triazole).

PSBE (4.13) (Synthesised from soybean oil): The general procedure for the polymerisation of the monomers was applied using **SBE 4.7**. ν_{max}/cm^{-1} 3351 (O-H), 2923 (C-H), 2853 (C-H), 2103 ($N=N^{+}=N^{-}$), 1735 (C=O), 1558 (C=C triazole), 1457 (N=N triazole).

PExOE (4.16): The general procedure for the polymerisation of the monomers was applied using **ExOE 4.8**. ν_{max}/cm^{-1} 3311 (O-H), 2924 (C-H), 2854 (C-H), 1731 (C=O), 1552 (C=C triazole), 1458 (N=N triazole).

PExLE (4.16): The general procedure for the polymerisation of the monomers was applied using **ExLE 4.8**. ν_{max}/cm^{-1} 3350 (O-H), 2926 (C-H), 2855 (C-H), 2102 ($N=N^{+}=N^{-}$), 1731 (C=O), 1554 (C=C triazole), 1458 (N=N triazole).

PExRSE (4.16) (Synthesised from rapeseed oil): The general procedure for the polymerisation of the monomers was applied using **ExRSE 4.8**. ν_{max}/cm^{-1} 3359 (O-H), 2924 (C-H), 2854 (C-H), 2100 ($N=N^{+}=N^{-}$), 1732 (C=O), 1551 (C=C triazole), 1458 (N=N triazole).

PExSBE (4.16) (Synthesised from soybean oil); The general procedure for the polymerisation of the monomers was applied using **ExSBE 4.8**. ν_{max}/cm^{-1} 3353 (O-H), 2926 (C-H), 2855 (C-H), 2102 ($N=N^{+}=N^{-}$), 1731 (C=O), 1554 (C=C triazole), 1458 (N=N triazole).

PExOA (4.19): The general procedure for the polymerisation of the monomers was applied using **ExOA 4.9**. ν_{max}/cm^{-1} 3294 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1735 (OC=O), 1643 (HNC=O), 1548 (C=C triazole), 1459 (N=N triazole).

PExLA (4.19): The general procedure for the polymerisation of the monomers was applied using **ExLA 4.9**. ν_{max}/cm^{-1} 3324 (N-H, O-H), 2925 (C-H), 2854 (C-H), 1734 (OC=O), 1641 (HNC=O), 1548 (C=C triazole), 1457 (N=N triazole).

PExRSA (4.19) (Synthesised from rapeseed oil): The general procedure for the polymerisation of the monomers was applied using **ExRSA 4.9**. ν_{max}/cm^{-1} 3288 (N-H, O-H), 2923 (C-H), 2853 (C-H), 2102 ($N=N^{+}=N^{-}$), 1735 (OC=O), 1644 (HNC=O), 1548 (C=C triazole), 1457 (N=N triazole).

PExSBA (4.19) (Synthesised from soybean oil): The general procedure for the polymerisation of the monomers was applied using **ExSBA 4.9**. ν_{max}/cm^{-1} 3321 (N-H, O-H), 2925 (C-H), 2854 (C-H), 2102 ($N=N^{+}=N^{-}$), 1734 (OC=O), 1641 (HNC=O), 1547 (C=C triazole), 1457 (N=N triazole).

PEtOA (4.24): The general procedure for the polymerisation of the monomers was applied using **EtOA 4.10**. ν_{max}/cm^{-1} 3294 (N-H, O-H), 2919 (C-H), 2851 (C-H), 1637 (C=O), 1543 (C=C triazole), 1457 (N=N triazole).

PEtLA (4.24): The general procedure for the polymerisation of the monomers was applied using **EtLA 4.10**. ν_{max}/cm^{-1} 3295 (N-H, O-H), 2923 (C-H), 2853 (C-H), 1643 (C=O), 1546 (C=C triazole), 1457 (N=N triazole).

PEtRSA (4.24) (Synthesised from rapeseed oil): The general procedure for the polymerisation of the monomers was applied using **EtRSA 4.10**. ν_{max}/cm^{-1} 3293 (N-H, O-H), 2919 (C-H), 2850 (C-H), 1637 (C=O), 1552 (C=C triazole), 1461 (N=N triazole).

PEtSBA (4.24) (Synthesised from soybean oil): The general procedure for the polymerisation of the monomers was applied using **EtSBA 4.10**. ν_{max}/cm^{-1} 3296 (N-H, O-H), 2922 (C-H), 2853 (C-H), 1643 (C=O), 1546 (C=C triazole), 1457 (N=N triazole).

PDEtOA (4.25): The general procedure for the polymerisation of the monomers was applied using **DEtOA 4.11**. ν_{max}/cm^{-1} 3350 (O-H), 3308 (≡C-H), 2923 (C-H), 2853 (C-H), 1626 (C=O), 1543 (C=C triazole), 1462 (N=N triazole).

PDEtLA (4.25): The general procedure for the polymerisation of the monomers was applied using **DEtLA 4.11**. ν_{max}/cm^{-1} 3311 (O-H, ≡C-H), 2923 (C-H), 2853 (C-H), 1622 (C=O), 1543 (C=C triazole), 1457 (N=N triazole).

PDEtRSA (4.25) (Synthesised from rapeseed oil): The general procedure for the polymerisation of the monomers was applied using **DEtRSA 4.11**. ν_{max}/cm^{-1} 3350

(O-H), 3312 (≡C-H), 2922 (C-H), 2853 (C-H), 1623 (C=O), 1544 (C=C triazole), 1461 (N=N triazole).

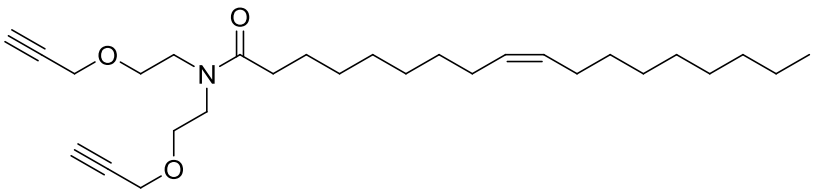
PDEtSBA polymer (4.25) (Synthesised from soybean oil): The general procedure for the polymerisation of the monomers was applied using **DEtSBA 4.11**. ν_{max}/cm^{-1} 3309 (O-H, ≡C-H), 2922 (C-H), 2853 (C-H), 1621 (C=O), 1543 (C=C triazole), 1457 (N=N triazole).

6.5 General Procedures in Chapter 5

6.5.1 General Procedure for the synthesis of propargyl unsaturated diethanolamine fatty amides

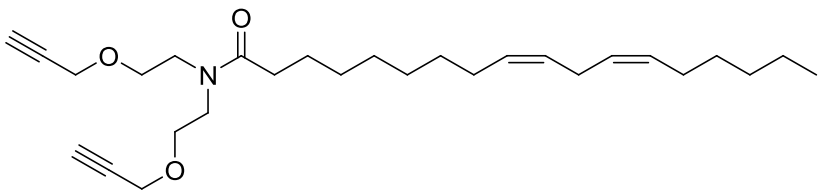
The desired unsaturated diethanolamine fatty amide (1.0 equiv.) was dissolved in dry THF (0.5 M) at -78 °C. Sodium hydride (95 %) (2.2 equiv.) was added and left to react for 30 mins. Propargyl bromide (80 wt. % in toluene) (2.2 equiv.) was added dropwise and the reaction mixture was left to warm to room temperature overnight. When complete the reaction mixture was quenched with aqueous acid (20 mL 2 M HCl) and extracted using Et_2O. The organic layer was washed with water (2 x 50 mL) then saturated NaCl (50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give pure product.

N,N-bis(2-(prop-2-ynyloxy)ethyl)oleamide (5.11)



The general procedure for the synthesis of propargyl unsaturated diethanolamine fatty amides was applied using **OA 4.20** (10.0 g, 27 mmol, 1.0 equiv.), NaH (1.5 g, 60 mmol, 2.2 equiv.) and propargyl bromide (5.3 mL, 60 mmol, 2.2 equiv) to give the product as a yellow oil. (59 %); ν_{max}/cm^{-1} 3307 (≡C-H), 2922 (C-H), 2852 (C-H), 2125 (C≡C), 1639 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.23 (m, 2H, *H*C=C*H*), 4.13 (dd, *J* = 8.9, 2.4 Hz, 4H, HC≡CC*H*$_2$O), 3.70 – 3.62 (m, 4H, OC*H*$_2$CH$_2$N), 3.62 – 3.55 (m, 4H, OCH$_2$C*H*$_2$N), 2.45 (dt, *J* = 12.4, 2.3 Hz, 2H, *H*C≡CCH$_2$O), 2.36 (t, *J* = 7.8 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.08 – 1.95 (m, 4H, =CHC*H*$_2$CH$_2$), 1.63 (p, *J* = 7.0 Hz, 2H, O=CCH$_2$C*H*$_2$), 1.43 – 1.18 (m, 20H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 3H, CH$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.66 (O=*C*CH$_2$CH$_2$), 130.08 (H*C*=*C*H), 129.99 (H*C*=*C*H), 129.85 (H*C*=*C*H), 129.72 (H*C*=*C*H), 128.72 (H*C*=*C*H), 127.92 (H*C*=*C*H), 127.86 (H*C*=*C*H), 127.39 (H*C*=*C*H), 79.59 (H*C*≡CCH$_2$O), 79.24 (H*C*≡CCH$_2$O), 74.78 (HC≡*C*CH$_2$O), 74.43 (HC≡*C*CH$_2$O), 68.60 (O*C*H$_2$CH$_2$N), 67.93 (O*C*H$_2$CH$_2$N), 58.38 (HC≡C*C*H$_2$O), 58.16 (H*C*≡CCH$_2$O), 48.71 (OCH$_2$*C*H$_2$N), 46.30 (OCH$_2$*C*H$_2$N), 32.98 (O=C*C*H$_2$CH$_2$), 31.83 (*C*H$_2$), 29.67 (*C*H$_2$), 29.57 (*C*H$_2$), 29.44 (*C*H$_2$), 29.33 (*C*H$_2$), 29.24 (*C*H$_2$), 29.12 (*C*H$_2$), 27.13 (=CH*C*H$_2$CH$_2$), 25.22 (O=CCH$_2$*C*H$_2$), 22.61 (*C*H$_2$), 14.05 (*C*H$_3$).; *m/z* (ES^+) 468.3 $[M+Na]^+$ (C18:1).

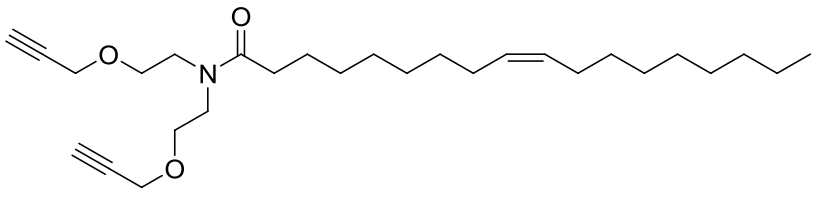
(9Z,12Z)-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadeca-9,12-dienamide (5.12)



The general procedure for the synthesis of propargyl unsaturated diethanolamine fatty amides was applied using **LA 4.20** (10.0 g, 27 mmol, 1.0 equiv.), NaH (1.5 g,

60 mmol, 2.2 equiv.) and propargyl bromide (5.3 mL, 60 mmol, 2.2 equiv) to give the product as a yellow oil. (60 %); ν_{max}/cm^{-1} 3306 (≡C-H), 2923 (C-H), 2852 (C-H), 2140 (C≡C), 1639 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.25 (m, 3H, *H*C=C*H*), 4.13 (dd, *J* = 9.2, 2.2 Hz, 4H, HC≡CC*H*$_2$O), 3.69 – 3.62 (m, 4H, OC*H*$_2$CH$_2$N), 3.62 – 3.54 (m, 4H, OCH$_2$C*H*$_2$N), 2.83 – 2.73 (m, 1H, =CHC*H*$_2$CH=), 2.46 (dt, *J* = 12.7, 2.1 Hz, 2H, *H*C≡CCH$_2$O), 2.36 (t, *J* = 7.6 Hz, 2H, O=CC*H*$_2$CH$_2$), 2.09 – 1.93 (m, 4H, =CHC*H*$_2$CH$_2$), 1.62 (p, *J* = 6.9 Hz, 2H, O=CCH$_2$C*H*$_2$), 1.41 – 1.20 (m, 17H, C*H*$_2$), 0.88 (dt, *J* = 6.9, 6.5, 4.0 Hz, 3H, C*H*$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.49 (O=*C*CH$_2$CH$_2$), 129.99 (H*C*=*C*H), 129.91 (H*C*=*C*H), 129.77 (H*C*=*C*H), 129.64 (H*C*=*C*H), 127.85 (H*C*=*C*H), 127.78 (H*C*=*C*H), 79.53 (H*C*≡CCH$_2$O), 79.18 (H*C*≡CCH$_2$O), 74.74 (HC≡*C*CH$_2$O), 74.39 (HC≡*C*CH$_2$O), 68.52 (O*C*H$_2$CH$_2$N), 67.87 (O*C*H$_2$CH$_2$N), 58.30 (HC≡C*C*H$_2$O), 58.08 (HC≡C*C*H$_2$O), 48.62 (OCH$_2$*C*H$_2$N), 46.22 (OCH$_2$*C*H$_2$N), 32.89 (O=C*C*H$_2$CH$_2$), 31.76 (*C*H$_2$), 31.37 (*C*H$_2$), 29.60 (*C*H$_2$), 29.50 (*C*H$_2$), 29.38 (*C*H$_2$), 29.26 (*C*H$_2$), 29.20 (*C*H$_2$), 29.17 (*C*H$_2$), 29.05 (*C*H$_2$), 27.05 (=CH*C*H$_2$CH$_2$), 25.48 (=CH*C*H$_2$CH=), 25.14 (O=CCH$_2$*C*H$_2$), 22.54 (*C*H$_2$), 22.43 (*C*H$_2$), 13.99 (*C*H$_3$), 13.95 (*C*H$_3$).; *m/z* (ES$^+$) 468.3 [M+Na]$^+$ (C18:1), 466.3 [M+Na]$^+$ (C18:2)

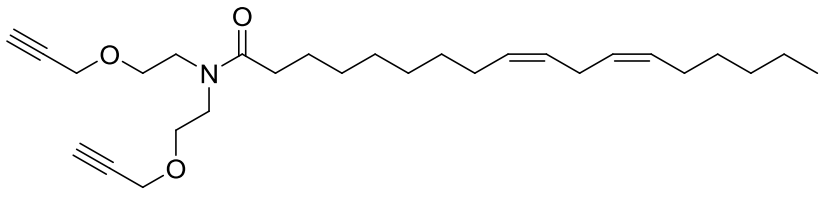
N,N-bis(2-(prop-2-ynyloxy)ethyl)oleamide (5.13) (synthesised from rapeseed oil)



The general procedure for the synthesis of propargyl unsaturated diethanolamine fatty amides was applied using **RSA 4.20** (10.0 g, 27 mmol, 1.0 equiv.), NaH (1.5 g, 60 mmol, 2.2 equiv.) and propargyl bromide (5.3 mL, 60 mmol, 2.2 equiv) to give

the product as a yellow oil. (61 %); ν_{max}/cm^{-1} 3306 (≡C-H), 2923 (C-H), 2853 (C-H), 2110 (C≡C), 1638 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.27 (m, 2H, *H*C=C*H*), 4.13 (dd, *J* = 9.3, 2.3 Hz, 4.4H, HC≡CC*H*$_2$O), 3.70 – 3.63 (m, 4H, OC*H*$_2$CH$_2$N), 3.63 – 3.56 (m, 4H, OCH$_2$C*H*$_2$N), 2.49 – 2.42 (m, 2.2H, *H*C≡CCH$_2$O), 2.38 (t, *J* = 7.8 Hz, 2H, NO=CCH$_2$CH$_2$), 2.31 (t, *J* = 7.5 Hz, 0.4H, OO=CC*H*$_2$CH$_2$), 2.10 – 1.94 (m, 3H, =CHC*H*$_2$CH$_2$), 1.66 – 1.57 (m, 2H, O=CCH$_2$C*H*$_2$), 1.40 – 1.20 (m, 21H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 3H, CH$_3$).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19 (O=*C*CH$_2$CH$_2$), 130.28 (H*C*=*C*H), 130.18 (H*C*=*C*H), 130.07 (H*C*=*C*H), 129.94 (H*C*=*C*H), 129.78 (H*C*=*C*H), 128.25 (H*C*=*C*H), 128.00 (H*C*=*C*H), 127.92 (H*C*=*C*H), 79.61 (H*C*≡CCH$_2$O), 79.27 (H*C*≡CCH$_2$O), 74.87 (HC≡*C*CH$_2$O), 74.52 (HC≡*C*CH$_2$O), 68.60 (O*C*H$_2$CH$_2$N), 67.92 (OCH$_2$CH$_2$N), 58.47 (HC≡C*C*H$_2$O), 58.25 (HC≡C*C*H$_2$O), 58.20 (HC≡C*C*H$_2$O), 48.88 (OCH$_2$*C*H$_2$N), 46.46 (OCH$_2$*C*H$_2$N), 33.05 (O=C*C*H$_2$CH$_2$), 31.89 (*C*H$_2$), 29.73 (*C*H$_2$), 29.68 (*C*H$_2$), 29.51 (*C*H$_2$), 29.38 (*C*H$_2$), 29.30 (*C*H$_2$), 29.18 (*C*H$_2$), 27.19 (=CH*C*H$_2$CH$_2$), 25.34 (O=CCH$_2$*C*H$_2$), 22.66 (*C*H$_2$), 14.64 (*C*H$_2$), 14.11 (*C*H$_3$).; *m/z* (ES^+) 468.3 $[M+Na]^+$ (C18:1), 466.3 $[M+Na]^+$ (C18:2)

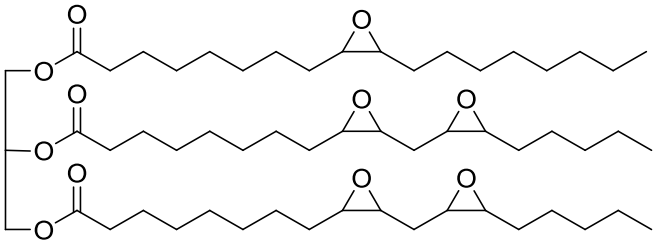
(9Z,12Z)-N,N-bis(2-(prop-2-ynyloxy)ethyl)octadeca-9,12-dienamide (5.14) (synthesised from soybean oil)



The general procedure for the synthesis of propargyl unsaturated diethanolamine fatty amides was applied using **SBA 4.20** (10.0 g, 27 mmol, 1.0 equiv.), NaH (1.5 g, 60 mmol, 2.2 equiv.) and propargyl bromide (5.3 mL, 60 mmol, 2.2 equiv) to give

the product as a yellow oil. (62 %); ν_{max}/cm^{-1} 3291 (≡C-H), 2924 (C-H), 2853 (C-H), 2110 (C≡C), 1637 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 – 5.23 (m, 3H, *H*C=C*H*), 4.14 (dd, *J* = 9.2, 2.3 Hz, 5H, HC≡CCH_2O), 3.71 – 3.63 (m, 4H, OCH_2CH_2N), 3.63 – 3.56 (m, 4H, OCH_2CH_2N), 2.44 (tt, *J* = 4.7, 2.5 Hz, 2.5H, HC≡CCH_2O), 2.41 – 2.35 (m, 2H, NO=CCH_2CH_2), 2.35 – 2.29 (m, 1H, OOCCH_2CH_2), 2.10 – 1.96 (m, 1H, =CHCH_2CH=), 1.67 – 1.57 (m, 2H, O=CCH_2CH_2), 1.40 – 1.21 (m, 18H, CH_2), 0.88 (dt, *J* = 7.0, 6.2, 4.0 Hz, 3H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.37 (O=*C*CH_2CH_2), 130.28 (H*C*=*C*H), 130.16 (H*C*=*C*H), 130.03 (H*C*=*C*H), 129.86 (H*C*=*C*H), 128.08 (H*C*=*C*H), 127.99 (H*C*=*C*H), 79.68 (H*C*≡CCH_2O), 79.33 (H*C*≡CCH_2O), 74.92 (HC≡*C*CH_2O), 74.57 (HC≡*C*CH_2O), 68.67 (O*C*H_2CH_2N), 68.52 (O*C*H_2CH_2N), 58.56 (HC≡C*C*H_2O), 58.34 (HC≡C*C*H_2O), 58.29 (HC≡C*C*H_2O), 48.98 (OCH_2*C*H_2N), 46.55 (OCH_2*C*H_2N), 33.13 (O=C*C*H_2CH_2), 31.96 (*C*H_2), 31.58 (*C*H_2), 29.82 (*C*H_2), 29.75 (*C*H_2), 29.71 (*C*H_2), 29.38 (*C*H_2), 29.26 (*C*H_2), 27.27 (=CH*C*H_2CH_2), 25.69 (*C*H_2), 25.43 (O=CCH_2*C*H_2), 24.80 (*C*H_2), 22.74 (*C*H_2), 22.63 (*C*H_2), 14.71 (*C*H_3), 14.19 (*C*H_3).; *m/z* (ES^+) 468.3 $[M+Na]^+$ (C18:1), 466.3 $[M+Na]^+$ (C18:2)

6.5.2 Synthesis of epoxidised soybean oil (2.1)



Soybean oil (20.0 g, 23 mmol, 1.0 equiv.) was dissolved in toluene (30 mL, 0.75 M) at 80 °C. Amberlite (5 g, 25 wt%) and acetic acid (0.7 g, 12 mmol, 0.5 equiv) were added followed by 30 % hydrogen peroxide (11.0 mL, 184 mmol, 8.0 equiv) dropwise and stirred at 80 °C for 4 hours. The reaction mixture was diluted with

ethyl acetate, Amberlite was filtered off and the filtrate was washed with water (3 x 100 mL) then with saturated NaCl (1 x 100 mL). The organic layer was dried over $MgSO_4$ and solvent removed *in vacuo* to give pure product as a pale yellow oil (96 %).; ν_{max}/cm^{-1} 2923 (C-H), 2853 (C-H), 1739 (C=O).; ^1H NMR (300 MHz, $CDCl_3$) δ 5.28 – 5.16 (m, 1H, $OCH_2CH(O)CH_2O$), 4.19 (ddd, *J* = 17.8, 11.9, 5.1 Hz, 4H, $OCH_2CH(O)CH_2O$), 3.38 – 2.80 (m, 8H, $HC(O)CH$), 2.28 (t, *J* = 7.5 Hz, 6H, $O=CCH_2CH_2$), 1.81 – 1.66 (m, 3H, $(O)CHCH_2CH(O)$), 1.63 – 1.54 (m, 6H, $O=CCH_2CH_2$), 1.53 – 1.41 (m, 12H, $CH_2CH(O)$), 1.40 – 1.09 (m, 44H, CH_2), 0.86 (dt, *J* = 6.9 Hz, 9H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.28 ($O=CCH_2CH_2$), 172.87 ($O=CCH_2CH_2$), 68.96 ($OCH_2CH(O)CH_2O$), 62.15 ($OCH_2CH(O)CH_2O$), 57.29 ($HC(O)CH$), 57.24 ($HC(O)CH$), 57.09 ($HC(O)CH$), 57.02 ($HC(O)CH$), 56.81 ($HC(O)CH$), 56.73 ($HC(O)CH$), 54.42 ($HC(O)CH$), 54.26 ($HC(O)CH$), 34.20 ($O=CCH_2CH_2$), 34.04 ($O=CCH_2CH_2$), 31.98 (CH_2), 31.92 (CH_2), 31.74 (CH_2), 29.76 (CH_2), 29.60 ($CH_2CH(O)CHCH_2$), 29.54 (CH_2), 29.42 (CH_2), 29.37 (CH_2), 29.26 (CH_2), 29.17 (CH_2), 29.05 (CH_2), 27.94 (CH_2), 27.87 (CH_2), 27.27 (CH_2), 26.98 (CH_2), 26.67 (CH_2), 26.31 (CH_2), 26.20 (CH_2), 24.86 ($O=CCH_2CH_2$), 22.73 (CH_2), 22.63 (CH_2), 14.18 (CH_3), 14.06 (CH_3).; *m/z* (ES^+) 983.7 $[M+Na]^+$ (2 x C18:2, C18:1) 964.8 $[M+Na]^+$ (C18:2, 2 x C18:1).

6.5.3 Synthesis of propargyl ring-opened soybean oil (3.1)

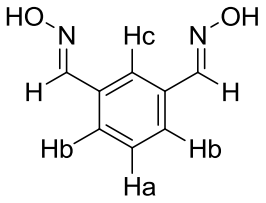
Epoxidised soybean oil (20 g) and propargyl alcohol (30.8g, 5equiv./epoxide) were dissolved in DCM (300ml). $BF_3.Et_2O$ (261µL, 0.1eq) was added dropwise and the solution was stirred at RT for 10 mins followed by quenching with saturated sodium hydrogen carbonate solution (200 mL). The mixture was extracted with DCM (2 x 100 mL) and the combined organic layers dried over $MgSO_4$ and solvent removed in vacuo to give crude product which was purified through silica plug (diethyl ether) to

give the pure product as a orange viscous oil (90 %).; ν_{max}/cm^{-1} 3469 (O-H), 3308 (≡C-H), 2923 (C-H), 2853 (C-H), 1739 (C=O),; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.22 (m, 1H, $OCH_2CH(O)CH_2O$), 4.42 – 3.99 (m, 9H, , $OCH_2CH(O)CH_2O$, $HC{\equiv}CCH_2O$), 3.89 – 3.28 (m, 8H, $CH_2CH(OR)$, $CH_2CH(OH)$), 2.46 – 2.39 (m, 2.5H, $HC{\equiv}CCH_2O$), 2.31 (t, *J* = 7.5 Hz, 6H, $O{=}CCH_2CH_2$), 1.68 – 1.54 (m, 11H, $O{=}CCH_2CH_2$, CH_2), 1.52 – 1.20 (m, 59H, $CH_2CH(OR)$, $CH_2CH(OH)$, CH_2), 0.88 (dt, *J* = 10.6, 6.1 Hz, 9H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.34 ($O{=}CCH_2CH_2$), 172.92 ($O{=}CCH_2CH_2$), 82.39 ($CH_2CH(OH)$), 82.32 ($CH_2CH(OH)$), 82.24 ($CH_2CH(OH)$), 74.41 ($HC{\equiv}CCH_2O$), 72.61 ($CH_2CH(OR)$), 71.95 ($HC{\equiv}CCH_2O$), 68.97 ($OCH_2CH(O)CH_2O$), 62.16 ($OCH_2CH(O)CH_2O$), 57.61 ($HC{\equiv}CCH_2O$), 57.56 ($HC{\equiv}CCH_2O$), 34.22 ($O{=}CCH_2CH_2$), 34.06 ($O{=}CCH_2CH_2$), 33.38 (CH_2), 31.99 (CH_2), 30.12 (CH_2), 29.96 (CH_2), 29.76 (CH_2), 29.73 (CH_2), 29.55 (CH_2), 29.43 (CH_2), 29.34 (CH_2), 29.18 (CH_2), 29.10 (CH_2), 27.12 (CH_2), 25.80 (CH_2), 25.14 ($O{=}CCH_2CH_2$), 24.93 (CH_2), 22.74 (CH_2), 22.63 (CH_2), 14.20 (CH_3), 14.12 (CH_3).; *m/z* (ES^+) 1263.8 $[M+Na]^+$ (2 x C18:2, C18:1), 1193.8 $[M+Na]^+$ (C18:2, 2 x C18:1), 1164.8 $[M+Na]^+$ (2 x C18:2, C18:1, 3 propargyl groups), 1132.8 [M+Na]+ (C18:2, 2 x C18:1, 3 propargyl groups),

6.5.4 General procedure for the synthesis of benzaldehyde dioxime

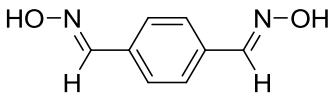
The desired phthalaldehyde (1 equiv.) was dissolved in ethanol:water (0.2 M, 1:1) at RT. Sodium acetate (2.2 equiv.) and hydroxylamine hydrochloride (2.2 equiv.) were added and left to stir at room temperature. Precipitate forms after 15 mins however the reaction was left for 4 hours. The reaction mixture was filtered using vacuum filtration and precipitate was washed with ethanol and left on vacuum until dry to give pure product.

(1E,1'E)-3-((E)-(hydroxyimino)methyl)benzaldehyde oxime (5.16)



The general procedure for the synthesis of benzaldehyde dioxime was applied using isophthalaldehyde **5.15a** (5.0 g, 37 mmol, 1.0 equiv.), sodium acetate (11.2 g, 82 mmol, 2.2 equiv.) and hydroxylamine hydrochloride (5.7 g, 82 mmol, 2.2 equiv) to give the product as a cream solid. (90 %); ν_{max}/cm^{-1} 3050 (C-H), 1622 (C=N); ^{1}H NMR (300 MHz, Acetone) δ 10.53 (s, 2H, O*H*), 8.17 (s, 2H, C*H*N(OH)), 7.88 (s, 1H Ar*Hc*), 7.62 (dd, *J* = 7.7, 1.2 Hz, 2H, Ar*Hb*), 7.42 (t, *J* = 7.7 Hz, 1H, Ar*Ha*).; ^{13}C NMR (75 MHz, Acetone) δ 148.94 (*C*HN(OH)), 134.67 (Ar*C*), 129.83 (Ar*C*Ha), 128.22 (Ar*C*Hb), 125.41 (Ar*C*Hc).; *m/z* (ES^{+}) 187.0 $[M+Na]^{+}$

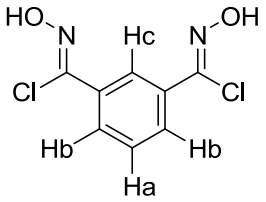
(1E,1'E)-4-((E)-(hydroxyimino)methyl)benzaldehyde oxime 5.17



The general procedure for the synthesis of benzaldehyde dioxime was applied using terephthalaldehyde **5.15b** (5.0 g, 37 mmol, 1.0 equiv.), sodium acetate (11.2 g, 82 mmol, 2.2 equiv.) and hydroxylamine hydrochloride (5.7 g, 82 mmol, 2.2 equiv) to give the product as a cream solid. (80 %); ν_{max}/cm^{-1} 3052 (C-H), 1623 (C=N); ^{1}H NMR (300 MHz, Acetone) δ 10.53 (s, 2H, O*H*), 8.15 (s, 2H, C*H*N(OH)), 7.64 (s, 4H, Ar*H*).; ^{13}C NMR (75 MHz, Acetone) δ 148.93 (*C*HN(OH)), 135.09 (Ar*C*), 127.68 (Ar*C*H).; *m/z* (ES^{+}) 187.0 $[M+Na]^{+}$

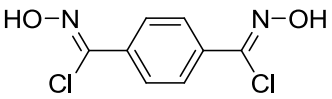
6.5.5 General procedure for the synthesis of benzaldehyde dioximoyl chloride: The desired benzaldehyde dioxime (1 equiv.) was dissolved in DMF (3.0 M) at RT. *N*-Chlorosuccinimide (2.2 equiv.) was added and left to stir at room temperature for 2 hours. The reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (50 mL). The organic layer was washed with water (2 x 50 mL), saturated sodium thiosulfate (50 mL) finally saturated NaCl (50 mL). The organic layer was dried over $MgSO_4$ and solvent removed *in vacuo* to give pure product.

(1Z,3Z)-N'1,N'3-dihydroxyisophthalimidoyl dichloride (5.1)



The general procedure for the synthesis of benzaldehyde dioximoyl chloride was applied using **5.16** (4.0 g, 24 mmol, 1.0 equiv.), and *N*-Chlorosuccinimide (7.2 g, 53 mmol, 2.2 equiv) to give the product as a cream solid. (96 %); ν_{max}/cm^{-1} 3405 (O-H), 3033 (C-H), 1656 (C=N).; ^{1}H NMR (300 MHz, Acetone) δ 8.32 (s, 1H, Ar*Hc*), 7.93 (dd, *J* = 7.9, 1.7 Hz, 2H, Ar*Hb*), 7.55 (t, *J* = 7.9 Hz, 1H, Ar*Ha*).; ^{13}C NMR (75 MHz, Acetone) δ 163.57 (HON=*C*Cl), 136.66 (Ar*C*), 134.67 (Ar*C*), 130.09 (Ar*C*Ha), 129.48 (Ar*C*Hb), 125.90 (Ar*C*Hc).; *m/z* (ES^{+}) 254.9 $[M+Na]^{+}$

(1Z,4Z)-N'1,N'4-dihydroxyterephthalimidoyl dichloride (5.10)



The general procedure for the synthesis of benzaldehyde dioximoyl chloride was applied using **5.17** (4.0 g, 24 mmol, 1.0 equiv.), and *N*-Chlorosuccinimide (7.2 g, 53

mmol, 2.2 equiv) to give the product as a cream solid. (92 %); ν_{max}/cm^{-1} 3406 (O-H), 3034 (C-H), 1661 (C=N).; ^{1}H NMR (300 MHz, Acetone) δ 11.62 (s, 2H, *H*ON=CCl), 7.93 (s, 4H, Ar*H*).; ^{13}C NMR (75 MHz, Acetone) δ 164.67 (HON=*C*Cl), 136.93 (Ar*C*), 135.51 (Ar*C*), 127.74 (Ar*C*H).; *m/z* (ES^{+}) 254.9 $[M+Na]^{+}$

6.5.6 General procedure for base mediated polymerisation

The desired dialkyne/polyalkyne (1.0 equiv.) was dissolved in DCM:water (4:1, 0.5 M) at RT. Tetrabutylamminium bromide (TBAB) (0.05 equiv.) and NaOH (2.0 equiv. (4.5 equiv. for polyalkyne)) were added followed by the nitrile oxide precursor (1.0 equiv. (2.25 equiv for polyalkyne)). The reaction mixture was stirred at RT in a sealed tube for 24 hours after which reaction mixture was dried in a 30 °C oven overnight to give the desired polymer.

P^{B}_{META}(DAOA) 5.18: The general procedure for base mediated polymerisation was applied using **5.11** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.1** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3303 (≡C-H), 2922 (C-H), 2852 (C-H), 1685 (C=N), 1634 (C=O) 1102 (C-O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (br s, 1H, Ar*H*), 7.84 (br s, 2H, Ar*H*), 7.50 (br s, 1H, Ar*H*), 6.57 (br s, 2H C*H* isoxazole), 5.36 (br s, 2H, *H*C=C*H*), 4.61 (br s, 3H, HC=CCH_2O), 4.11 (br s, 2H, HC≡CCH_2O), 3.75 – 3.51 (br m, 10H, ROCH_2CH_2N), 3.29 (br s, 1H, C*H* isoxazoline), 2.36 (br s, 4H, O=CCH_2CH_2, *H*C≡CCH_2O), 1.96 (br s, 4H, =CHCH_2), 1.52 (br s, 4H, O=CCH_2CH_2, C*H* isoxazoline), 1.23 (br s, 25H, CH_2), 0.90 (dt, *J* = 10.4, 6.6 Hz, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.02 (O=*C*CH_2CH_2), 169.86 (quaternary *C*=N isoxazole), 161.84 (quaternary *C*=CH isoxazole), 130.01 (Ar*C*H), 129.84 (HC=CH), 129.73 (HC=CH), 129.34 (HC=CH), 128.38 (Ar*C*H), 125.20 (Ar*C*H), 101.29 (*C*H isoxazole), 69.78 (ROCH$_2$CH$_2$N), 69.49 (ROCH$_2$CH$_2$N), 68.74 (ROCH$_2$CH$_2$N),

68.10 (RO*C*$H_2$$CH_2$N) 64.13 (HC=C*C*$H_2$O), 63.83 (HC=C*C*$H_2$O), 58.97 (HC≡C*C*$H_2$O), 58.55 (HC≡C*C*$H_2$O), 58.33 (HC≡C*C*$H_2$O), 46.57 (ROCH$_2$*C*$H_2$N), 46.43 (ROCH$_2$*C*$H_2$N), 33.23 (O=C*C*$H_2$$CH_2$), 31.95 (*C*$H_2$), 29.81 (*C*$H_2$), 29.58 (*C*$H_2$), 29.48 (*C*$H_2$), 29.37 (*C*$H_2$), 29.26 (*C*$H_2$), 27.27 (=CH*C*$H_2$), 25.35 (*C*$H_2$), 24.08 (*C*$H_2$), 22.74 (*C*$H_2$), 14.20 (*C*$H_3$).

P$^{B}_{META}$(DALA) 5.19: The general procedure for base mediated polymerisation was applied using **5.12** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.1** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3304 (≡C-H), 2923 (C-H), 2853 (C-H), 1684 (C=N), 1631 (C=O) 1101 (C-O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (br s, 1H, Ar*H*), 7.87 (br s, 2H, Ar*H*), 7.52 (br s, 1H, Ar*H*), 6.62 (br s, 2H, C*H* isoxazole), 5.35 (br s, 2H, *H*C=C*H*), 4.64 (br s, 4H, HC=CC*H*$_2$O), 4.14 (br s, 2H, HC≡CC*H*$_2$O), 3.79 – 3.52 (br m, 11H, ROC*H*$_2$C*H*$_2$N), 3.37 – 3.24 (br m, 1H, C*H* isoxazoline), 2.48 – 2.25 (br m, 5H, O=CC*H*$_2$$CH_2$, *H*C≡C$CH_2$O), 2.00 (br s, 3H, =CHC*H*$_2$), 1.61 (br s, 4H, O=CC*H*$_2$$CH_2$, C*H* isoxazoline), 1.42 – 1.07 (br m, 24H, C*H*$_2$), 1.03 – 0.71 (br m, 6H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.04 (O=*C*$CH_2$$CH_2$), 169.88 (quaternary *C*=N isoxazole), 161.87 (quaternary *C*=CH isoxazole), 130.34 (H*C*=*C*H), 130.21 (H*C*=*C*H), 130.06 (Ar*C*H), 129.90 (H*C*=*C*H), 129.79 (H*C*=*C*H), 129.39 (H*C*=*C*H), 128.44 (Ar*C*H), 128.02 (H*C*=*C*H), 125.25 (Ar*C*H), 101.32 (*C*H isoxazole), 69.56 (RO*C*$H_2$$CH_2$N), 68.80 (RO*C*$H_2$$CH_2$N), 68.17 (RO*C*$H_2$$CH_2$N), 64.19 (HC=C*C*$H_2$O), 63.90 (HC=C*C*$H_2$O), 58.61 (HC≡C*C*$H_2$O), 58.39 (HC≡C*C*$H_2$O), 46.63 (ROCH$_2$*C*$H_2$N), 33.22 (O=C*C*$H_2$$CH_2$), 32.02 (*C*$H_2$), 29.87 (*C*$H_2$), 29.55 (*C*$H_2$), 29.43 (*C*$H_2$), 29.33 (*C*$H_2$), 27.33 (=CH*C*$H_2$), 25.41 (*C*$H_2$), 22.80 (*C*$H_2$), 14.25 (*C*$H_3$), 14.11 (*C*$H_3$).

P^{B}_{META}(DARSA) 5.20: The general procedure for base mediated polymerisation was applied using **5.13** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.1** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3289 (≡C-H), 2923 (C-H), 2853 (C-H), 1687 (C=N), 1632 (C=O) 1101 (C-O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (br s, 1H, Ar*H*), 7.87 (br s, 2H, Ar*H*), 7.54 (br s, 1H, Ar*H*), 6.63 (br s, 2H, C*H* isoxazole), 5.34 (br s, 2H, *H*C=C*H*), 4.64 (br s, 4H, HC=CCH_2O), 4.20 – 4.04 (br m, 4H, HC≡CCH_2O), 3.78 – 3.44 (br m, 14H, ROCH_2CH_2N), 3.27 – 3.15 (br m, 1H, C*H* isoxazoline), 2.48 – 2.24 (br m, 4H, O=CCH_2CH_2, HC≡CCH_2O), 2.00 (br s, 3H, =CHCH_2), 1.61 (br s, 4H, O=CCH_2*C*H_2, C*H* isoxazoline), 1.26 (br s, 29H, CH_2), 1.00 – 0.73 (br m, 6H, C*H*3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.98 (O=*C*CH_2CH_2), 169.90 (quaternary *C*=N isoxazole), 161.72 (quaternary *C*=CH isoxazole), 129.90 (H*C*=*C*H), 129.74 (Ar*C*H), 129.82 (H*C*=*C*H), 129.24 (H*C*=*C*H), 128.27 (Ar*C*H), 125.09 (Ar*C*H), 101.16 (*C*H isoxazole), 69.61 (RO*C*H_2CH_2N), 69.35 (RO*C*H_2CH_2N), 68.57 (RO*C*H_2CH_2N), 67.93 (RO*C*H_2CH_2N), 63.98 (HC=C*C*H_2O), 63.77 (HC=C*C*H_2O), 58.62 (HC≡C*C*H_2O), 58.43 (HC≡C*C*H_2O), 58.21 (HC≡C*C*H_2O), 48.85 (ROCH$_2$*C*H_2N), 48.75 (ROCH$_2$*C*H_2N), 46.44 (ROCH$_2$*C*H_2N), 33.05 (O=C*C*H_2CH_2), 31.85 (*C*H_2), 29.71 (*C*H_2), 29.47 (*C*H_2), 29.36 (*C*H_2), 29.26 (*C*H_2), 29.15 (*C*H_2), 27.16 (=CH*C*H_2), 25.26 (*C*H_2), 23.75 (*C*H_2), 22.64 (*C*H_2), 19.57 (*C*H_2), 14.62 (*C*H_3), 14.10 (CH_3) 13.52 (*C*H_3).

P^{B}_{META}(DASBA) 5.21: The general procedure for base mediated polymerisation was applied using **5.14** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.1** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3293 (≡C-H), 2924 (C-H), 2853 (C-H), 1687 (C=N), 1632 (C=O) 1101 (C-O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (br s, 1H, Ar*H*), 7.89

(br s, 2H, Ar*H*), 7.54 (br s, 1H, Ar*H*), 6.63 (br s, 2H, C*H* isoxazole), 5.34 (br s, 2H, *H*C=C*H*), 4.65 (br s, 4H, HC=CCH_2O), 4.15 (br s, 4H, HC≡CCH_2O), 3.81 – 3.42 (br m, 14H, ROCH_2CH_2N), 3.27 – 3.16 (br m, 1H, C*H* isoxazoline), 2.48 – 2.23 (br m, 4H, O=CCH_2CH$_2$, *H*C≡CCH$_2$O), 2.03 (br s, 2H, =CHCH_2), 1.61 (br s, 4H, O=CCH$_2$CH_2, C*H* isoxazoline), 1.25 (br s, 25H, CH$_2$), 1.02 – 0.73 (br m, 6H, CH$_3$).; ^{13}C NMR (75 MHz, CDCl$_3$) δ 174.00 (O=*C*CH$_2$CH$_2$), 169.97 (quaternary *C*=N isoxazole), 161.83 (quaternary *C*=CH isoxazole), 130.27 (H*C*=*C*H), 130.14 (H*C*=*C*H), 130.00 (Ar*C*H), 129.84 (H*C*=*C*H), 129.70 (H*C*=*C*H), 129.33 (H*C*=*C*H), 128.37 (Ar*C*H), 128.04 (H*C*=*C*H), 127.96 (H*C*=*C*H) 125.20 (Ar*C*H), 101.24 (*C*H isoxazole), 69.75 (RO*C*H$_2$CH$_2$N), 69.46 (RO*C*H$_2$CH$_2$N), 68.71 (RO*C*H$_2$CH$_2$N), 68.51 (RO*C*H$_2$CH$_2$N), 68.03 (RO*C*H$_2$CH$_2$N), 64.04 (HC=C*C*H$_2$O), 63.87 (HC=C*C*H$_2$O), 58.76 (HC≡C*C*H$_2$O), 58.54 (HC≡C*C*H$_2$O), 58.31 (HC≡C*C*H$_2$O), 48.95 (ROCH$_2$*C*H$_2$N), 48.85 (ROCH$_2$*C*H$_2$N), 46.55 (ROCH$_2$*C*H$_2$N), 46.43 (ROCH$_2$*C*H$_2$N), 33.15 (O=C*C*H$_2$CH$_2$), 31.95 (*C*H$_2$), 31.56 (*C*H$_2$), 29.74 (*C*H$_2$), 29.57 (*C*H$_2$), 29.46 (*C*H$_2$), 29.37 (*C*H$_2$), 29.26 (*C*H$_2$), 27.25 (=CH*C*H$_2$), 25.67 (*C*H$_2$), 25.34 (*C*H$_2$), 23.86 (*C*H$_2$), 22.74 (*C*H$_2$), 22.62 (*C*H$_2$), 19.68 (*C*H$_2$), 14.71 (*C*H$_3$), 14.19 (*C*H$_3$), 13.62 (*C*H$_3$).

P$^{B}_{META}$(PASBO) 5.22: The general procedure for base mediated polymerisation was applied using **3.1** (0.5 g, 0.4 mmol, 1.0 equiv.), TBAB (0.007 g, 0.02 mmol, 0.05 equiv.), NaOH (0.08 g, 1.8 mmol, 4.5 equiv.) and nitrile oxide precursor **5.10** (0.22 g, 0.9 mmol, 2.25 equiv.).; ν_{max}/cm^{-1} 3407 (O-H), 2923 (C-H), 2853 (C-H), 1736 (C=O) 1090 (C-O).;

P$^{B}_{PARA}$(DAOA) 5.23: The general procedure for base mediated polymerisation was applied using **5.11** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1

mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3296 (≡C-H), 2922 (C-H), 2852 (C-H), 1684 (C=N), 1635 (C=O) 1103 (C-O).;

P^{B}_{PARA}(DALA) 5.24: The general procedure for base mediated polymerisation was applied using **5.12** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3303 (≡C-H), 2923 (C-H), 2853 (C-H), 1684 (C=N), 1634 (C=O) 1101 (C-O).;

P^{B}_{PARA}(DARSA) 5.25: The general procedure for base mediated polymerisation was applied using **5.13** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3281(≡C-H), 2923 (C-H), 2853 (C-H), 1688 (C=N), 1633 (C=O) 1102 (C-O).;;

P^{B}_{PARA}(DASBA) 5.26:, The general procedure for base mediated polymerisation was applied using **5.14** (0.5 g, 1.1 mmol, 1.0 equiv.), TBAB (g, 0.055 mmol, 0.05 equiv.) NaOH (0.09 g, 2.2 mmol, 2.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3281(≡C-H), 2923 (C-H), 2853 (C-H), 1687 (C=N), 1635 (C=O) 1102 (C-O).;

P^{B}_{PARA}(PASBO) 5.27: The general procedure for base mediated polymerisation was applied using **3.1** (0.5 g, 0.4 mmol, 1.0 equiv.), TBAB (0.007 g, 0.02 mmol, 0.05 equiv.), NaOH (0.08 g, 1.8 mmol, 4.5 equiv.) and nitrile oxide precursor **5.10** (0.22 g, 0.9 mmol, 2.25 equiv.).; ν_{max}/cm^{-1} 3407 (O-H), 2923 (C-H), 2853 (C-H), 1737 (C=O) 1089 (C-O).;

6.5.7 General procedure for thermal mediated polymerisation

The desired dialkyne/polyalkyne (1.0 equiv.) was dissolved in DMF (4:1, 0.5 M) at RT. Nitrile oxide precursor (1.0 equiv.) was added and reaction stirred at RT until fully dissolved when the reaction mixture was heated to 100 °C in an oven for 24 hours to give the desired polymer.

P^{T}_{META}(DAOA) 5.28: The general procedure for thermal mediated polymerisation was applied using **5.11** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3298 (≡C-H), 2922 (C-H), 2852 (C-H), 1705 (C=N), 1637 (C=O) 1101 (C-O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br s, 1H, Ar*H*), 7.89 (br s, 2H, Ar*H*), 7.53 (br s, 1H, Ar*H*), 6.63 (br s, 1H, C*H* isoxazole), 5.34 (br s, 3H, *H*C=C*H*), 4.64 (br s, 3H, HC=CCH_2O), 4.18 – 4.09 (br m, 3H, HC≡CCH_2O), 3.78 – 3.51 (br m, 11H, ROCH_2CH_2N), 2.47 – 2.26 (br m, 5H, O=CCH_2CH$_2$, HC≡CCH_2O), 2.00 (br s, 5H, =CHCH_2), 1.61 (br s, 4H, O=CCH$_2$CH_2), 1.26 (br s, 34H, CH_2), 0.88 (br s, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.96 (O=*C*CH$_2$CH$_2$), 169.84 (quaternary *C*=N isoxazole), 161.87 (quaternary *C*=CH isoxazole), 130.26 (H*C*=*C*H), 130.00 (H*C*=*C*H) 129.83 (Ar*C*H), 129.74 (H*C*=*C*H) 128.37 (Ar*C*H), 125.19 (Ar*C*H), 101.28 (*C*H isoxazole), 69.78 (ROCH$_2$CH$_2$N), 69.46 (ROCH$_2$CH$_2$N), 68.72 (ROCH$_2$CH$_2$N), 68.03 (ROCH$_2$CH$_2$N), 64.11 (HC=C*C*H$_2$O), 63.84 (HC=C*C*H$_2$O) 58.53 (HC≡C*C*H$_2$O), 58.32 (HC≡C*C*H$_2$O), 48.94 (ROCH$_2$*C*H$_2$N), 48.84 (ROCH$_2$*C*H$_2$N), 46.55 (ROCH$_2$*C*H$_2$N), 33.14 (O=C*C*H$_2$CH$_2$), 31.94 (*C*H$_2$), 29.88 (*C*H$_2$), 29.57 (*C*H$_2$), 29.46 (*C*H$_2$), 29.36 (*C*H$_2$), 29.25 (*C*H$_2$), 27.26 (=CH*C*H$_2$), 25.37 (*C*H$_2$) 22.73 (*C*H$_2$), 14.18 (*C*H$_3$).

P^{T}_{META}(DALA) 5.29: The general procedure for thermal mediated polymerisation was applied using **5.12** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3296 (≡C-H), 2923 (C-H), 2853 (C-H), 1688 (C=N), 1638 (C=O) 1101 (C-O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br s, 1H, Ar*H*), 7.88 (br s, 2H, Ar*H*), 7.51 (br s, 1H, Ar*H*), 6.62 (br s, 1H, C*H* isoxazole), 5.34 (br s, 3H, *H*C=C*H*), 4.65 (br s, 2H, HC=CCH_2O), 4.13 (br s, 3H, HC≡CCH_2O), 3.77 – 3.49 (br m, 11H, ROCH_2CH_2N), 2.49 – 2.24 (br m, 6H, O=CCH_2CH_2, HC≡CCH_2O), 2.00 (br s, 4H, =CHCH_2), 1.61 (br s, 4H, O=CCH_2CH_2), 1.40 – 1.12 (br m, 26H, CH_2), 0.88 (br s, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.74 (O=*C*CH_2CH_2), 167.65 (quaternary *C*=N isoxazole) 161.46 (quaternary *C*=CH isoxazole), 130.36 (H*C*=*C*H), 130.16 (H*C*=*C*H), 129.89 (Ar*C*H), 128.43 (H*C*=*C*H), 128.05 (Ar*C*H), 125.28 (Ar*C*H), 101.53 (*C*H isoxazole), 68.90 (RO*C*H_2CH_2N), 68.18 (RO*C*H_2CH_2N), 64.22 (HC=C*C*H_2O), 58.62 (HC≡C*C*H_2O), 46.52 (ROCH_2*C*H_2N), 33.23 (O=C*C*H_2CH_2), 32.03 (*C*H_2), 29.89 (*C*H_2), 29.82 (*C*H_2), 29.59 (*C*H_2), 29.56 (*C*H_2), 29.46 (*C*H_2), 29.34 (*C*H_2), 27.34 (=CH*C*H_2), 22.91 (*C*H_2), 14.22 (*C*H_3).

P^{T}_{META}(DARSA) 5.30: The general procedure for thermal mediated polymerisation was applied using **5.13** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3296(≡C-H), 2922 (C-H), 2852 (C-H), 1696 (C=N), 1636 (C=O) 1101 (C-O).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br s, 1H, Ar*H*), 7.87 (br s, 2H, Ar*H*), 7.54 (br s, 1H, Ar*H*), 6.63 (br s, 2H, C*H* isoxazole), 5.34 (br s, 2H, *H*C=C*H*), 4.65 (br s, 3H, HC=CCH_2O), 4.14 (br s, 3H, HC≡CCH_2O), 3.79 – 3.47 (br m, 11H, ROCH_2CH_2N), 2.48 – 2.25 (br m, 4H, O=CCH_2CH_2, *H*C≡CCH_2O), 2.00 (br s, 4H, =CHCH_2), 1.61 (br s, 4H, O=CCH_2CH_2), 1.26 (br s, 31H, CH_2), 0.88 (br s, 6H, CH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.06

(O=*C*CH_2CH_2), 170.06 (quaternary *C*=N isoxazole), 161.81 (quaternary *C*=CH isoxazole), 130.26 (H*C*=*C*H), 129.99 (Ar*C*H), 129.82 (H*C*=*C*H), 129.74 (H*C*=*C*H), 128.35 (Ar*C*H), 125.19 (Ar*C*H), 101.24 (*C*H isoxazole), 69.75 (RO*C*H_2CH_2N), 69.44 (RO*C*H_2CH_2N), 68.69 (RO*C*H_2CH_2N), 68.01 (RO*C*H_2CH_2N), 64.11 (HC=C*C*H_2O), 63.87 (HC=C*C*H_2O), 59.29 (HC≡C*C*H_2O), 58.52 (HC≡C*C*H_2O), 58.30 (HC≡C*C*H_2O), 48.93 (ROCH$_2$*C*H_2N), 48.84 (ROCH$_2$*C*H_2N), 46.53 (ROCH$_2$*C*H_2N), 33.14 (O=C*C*H_2CH_2), 31.93 (*C*H_2), 29.79 (*C*H_2), 29.74 (*C*H_2), 29.56 (*C*H_2), 29.45 (*C*H_2), 29.35 (*C*H_2), 29.24 (*C*H_2), 27.25 (=CH*C*H_2), 25.36 (*C*H_2), 24.90 (*C*H_2), 22.72 (*C*H_2), 14.69 (*C*H_3), 14.17 (*C*H_3).

P^{T}_{META}(DASBA) 5.31: The general procedure for thermal mediated polymerisation was applied using **5.14** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.1** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3269(≡C-H), 2923 (C-H), 2853 (C-H), 1697 (C=N), 1637 (C=O) 1101 (C-O).; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (br s, 1H, Ar*H*), 7.90 (br s, 2H, Ar*H*), 7.54 (br s, 1H, Ar*H*), 6.63 (br s, 2H, C*H* isoxazole), 5.34 (br s, 2H, *H*C=C*H*), 4.67 (br s, 3H, HC=CCH_2O), 4.15 (br s, 4H, HC≡CCH_2O), 3.80 – 3.44 (br m, 12H, ROCH_2CH_2N)), 2.48 – 2.19 (br m, 5H, O=CCH_2CH_2, *H*C≡CCH_2O), 2.02 (br s, 3H, =CHCH_2), 1.61 (br s, 5H, O=CCH_2CH_2), 1.51 – 1.02 (br m, 26H, CH_2), 0.88 (br s, 5H, CH_3).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.41 (O=*C*CH_2CH_2), 169.96 (quaternary *C*=N isoxazole) 161.94 (quaternary *C*=CH isoxazole), 130.34 (H*C*=*C*H), 130.12 (H*C*=*C*H), 129.76 (Ar*C*H), 128.43 (Ar*C*H), 128.01 (H*C*=*C*H) 125.32 (Ar*C*H), 101.33 (*C*H isoxazole), 69.89 (RO*C*H_2CH_2N), 68.72 (RO*C*H_2CH_2N), 68.11 (RO*C*H_2CH_2N), 63.95 (HC=C*C*H_2O), 58.60 (HC≡C*C*H_2O), 58.38 (HC≡C*C*H_2O), 48.99 (ROCH$_2$*C*H_2N), 48.91 (ROCH$_2$*C*H_2N), 46.63 (ROCH$_2$*C*H_2N), 46.48 (ROCH$_2$*C*H_2N), 33.23 (O=C*C*H_2CH_2), 32.04 (*C*H_2),

31.63 (*C*H_2) 29.81 (*C*H_2), 29.56 (*C*H_2), 29.44 (*C*H_2), 29.32 (*C*H_2), 29.23 (*C*H_2), 27.32 (=CH*C*H_2), 22.80 (*C*H_2), 14.25 (*C*H_3).

P^T_{META}(PASBO) 5.32:The general procedure for thermal mediated polymerisation was applied using **3.1** (0.5 g, 0.4 mmol, 1.0 equiv.) and nitrile oxide precursor **5.1** (0.22 g, 0.9 mmol, 2.25 equiv.).; ν_{max}/cm^{-1} 3405 (O-H), 2923 (C-H), 2853 (C-H), 1737 (C=O) 1088 (C-O).;

P^T_{PARA}(DAOA) 5.33: The general procedure for thermal mediated polymerisation was applied using **5.11** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 2922 (C-H), 2852 (C-H), 1703 (C=N), 1633 (C=O) 1097 (C-O).;

P^T_{PARA}(DALA) 5.34: The general procedure for thermal mediated polymerisation was applied using **5.12** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 2923 (C-H), 2853 (C-H), 1687 (C=N), 1631 (C=O) 1097 (C-O).;

P^T_{PARA}(DARSA) 5.35: The general procedure for thermal mediated polymerisation was applied using **5.13** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 2922 (C-H), 2852 (C-H), 1692 (C=N), 1649 (C=O) 1098 (C-O).;

P^T_{PARA}(DASBA) 5.36: The general procedure for thermal mediated polymerisation was applied using **5.14** (0.5 g, 1.1 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.26 g, 1.1 mmol, 1.0 equiv.).; ν_{max}/cm^{-1} 3265 (≡C-H), 2923 (C-H), 2853 (C-H), 1694 (C=N), 1639 (C=O) 1100 (C-O).;

P^{T}_{PARA}(PASBO) 5.37: The general procedure for thermal mediated polymerisation was applied using **3.1** (0.5 g, 0.4 mmol, 1.0 equiv.) and nitrile oxide precursor **5.10** (0.22 g, 0.9 mmol, 2.25 equiv.).; ν_{max}/cm^{-1} 3406 (O-H), 2924 (C-H), 2853 (C-H), 1736 (C=O) 1092 (C-O).;

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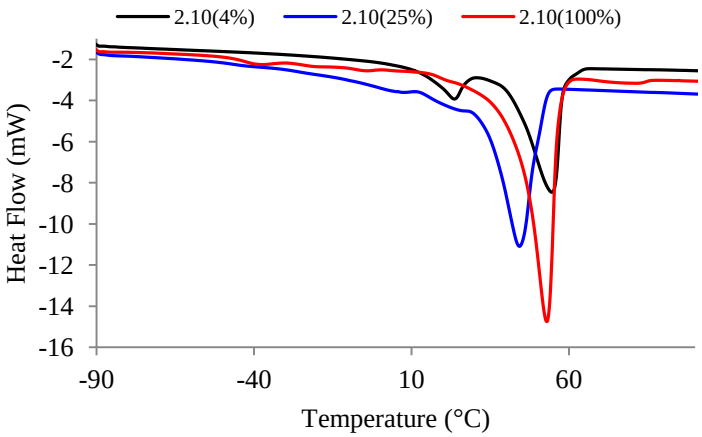
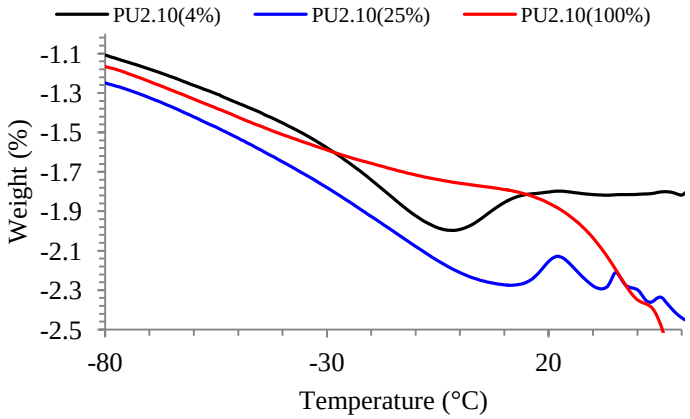
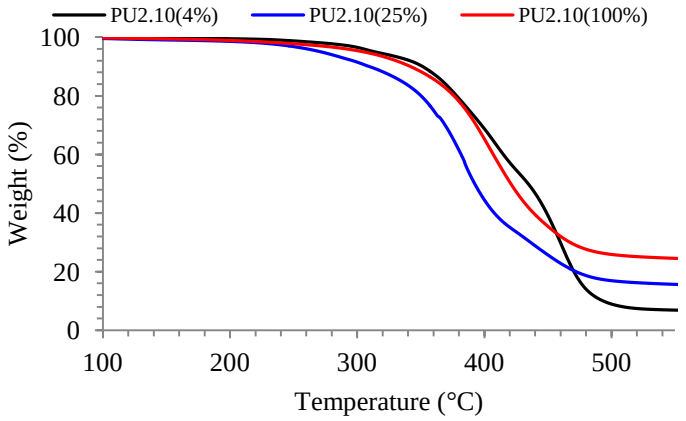
Appendix 1



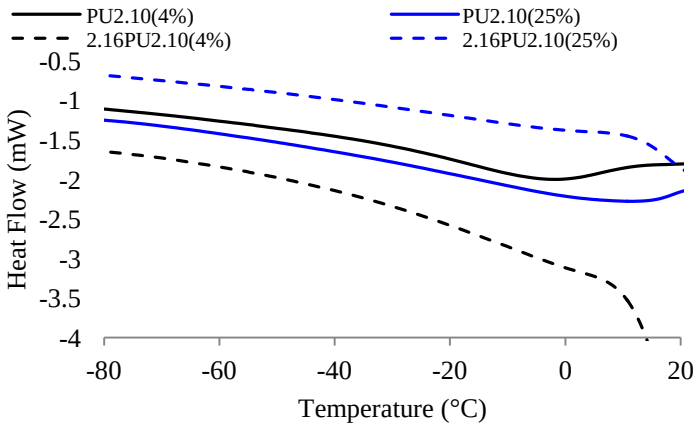
DSC of cocoa butter based monomers



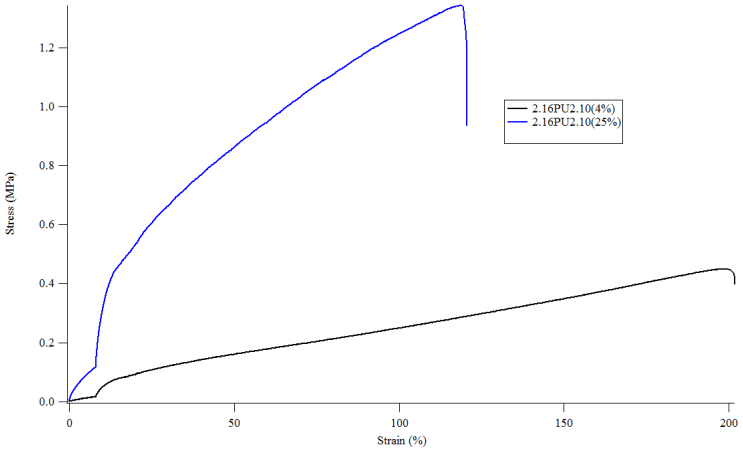
DSC of cocoa butter based polyurethanes



TGA of cocoa butter based polyurethanes.

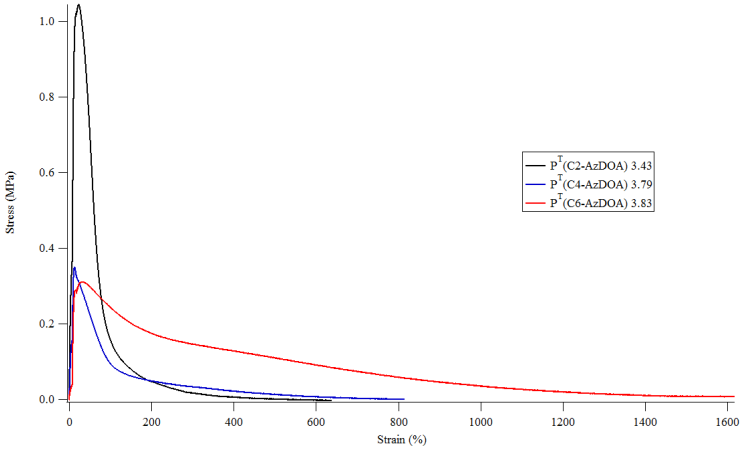


DSC of cocoa butter based polyurethanes with and without dye.

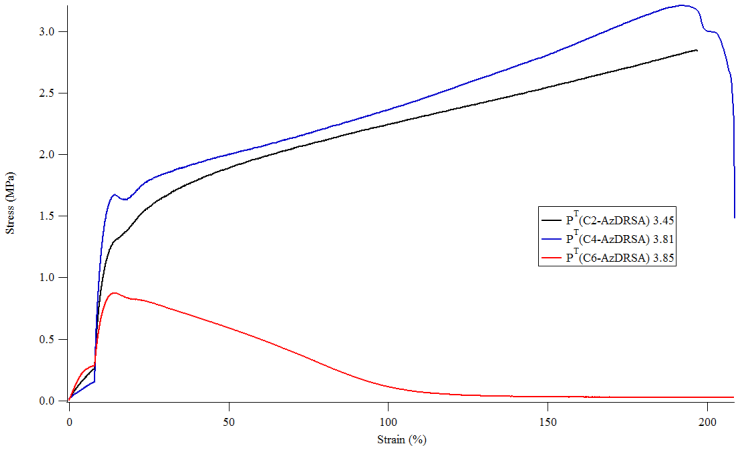


Stress strain curve of cocoa butter polyurethanes with dye.

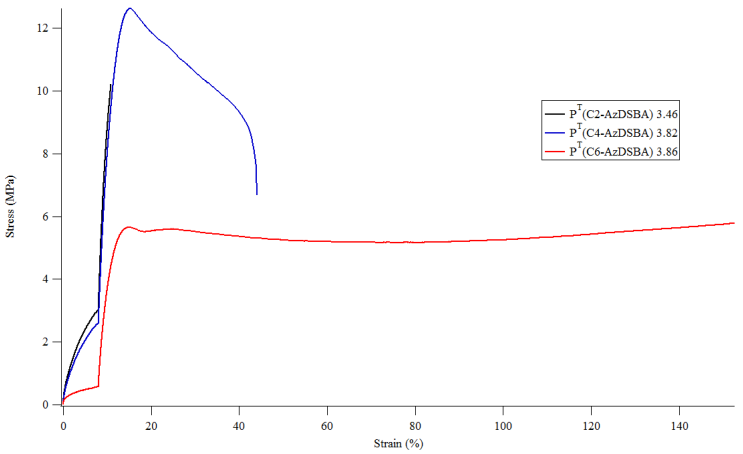
Appendix 2



Stress strain comparison of oleic series.

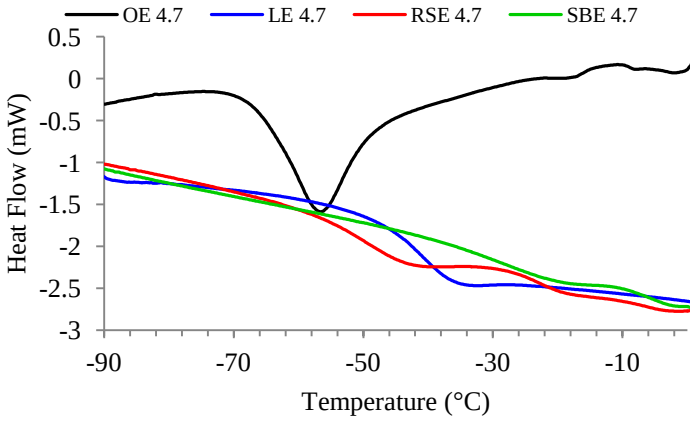


Stress strain comparison of Rapeseed oil series.

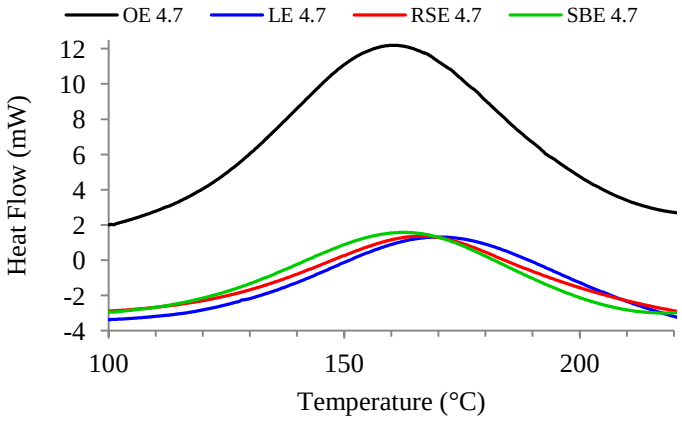


Stress strain comparison of soybean oil series.

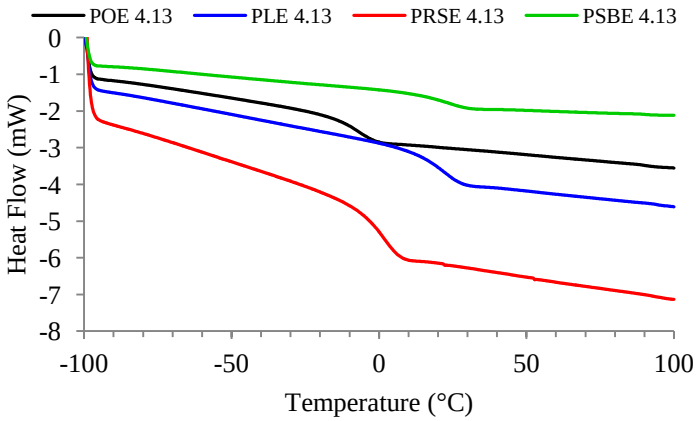
Appendix 3



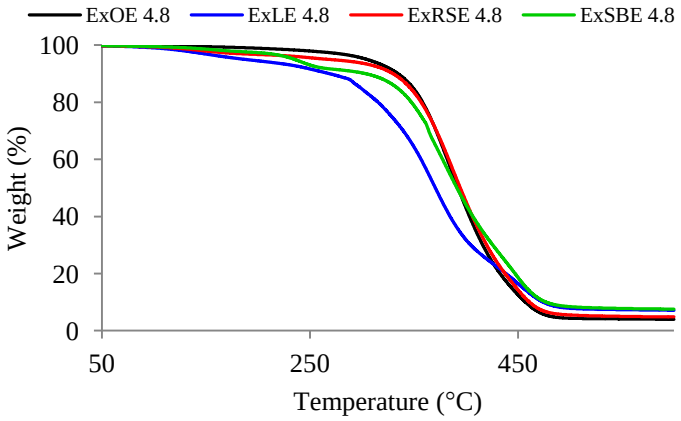
DSC of monomers 4.7 T_g.



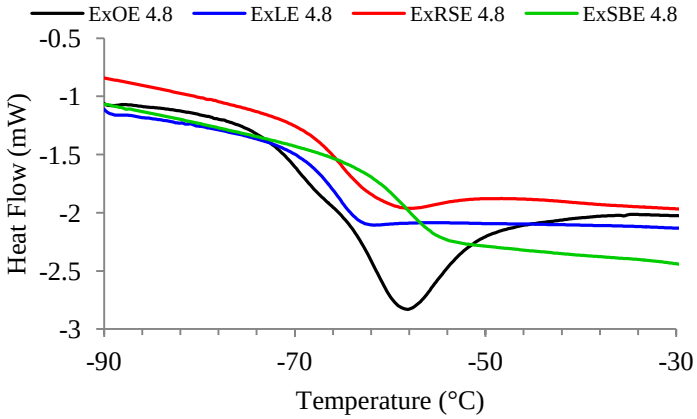
DSC of monomers 4.7 cure point.



DSC of PE polymers 4.13 T_g.



TGA of ExE monomers 4.8.



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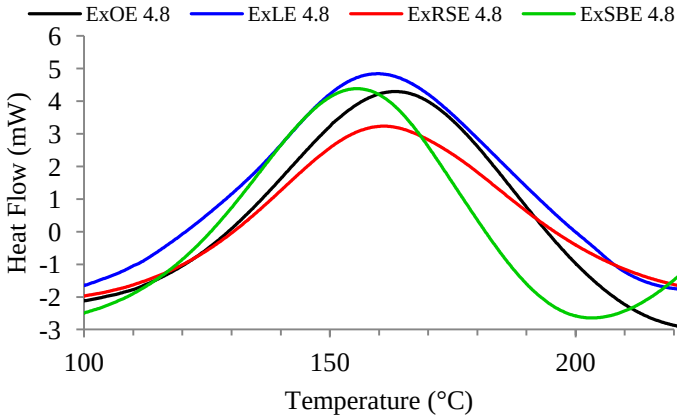

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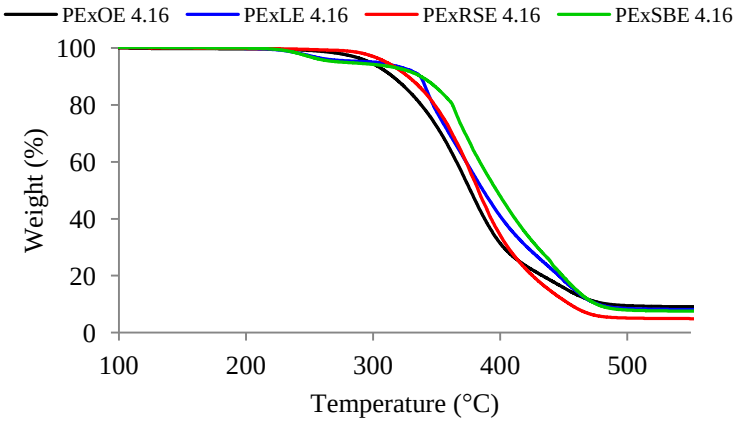
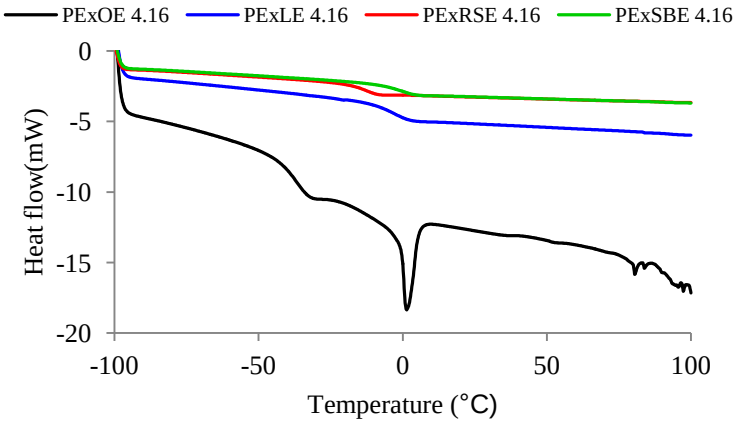
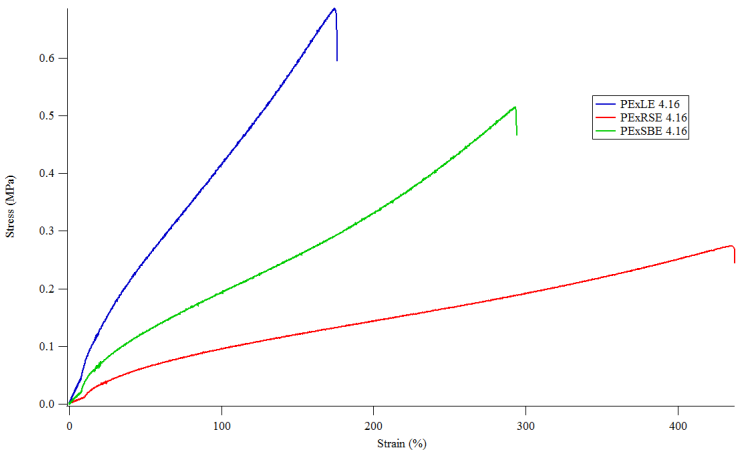


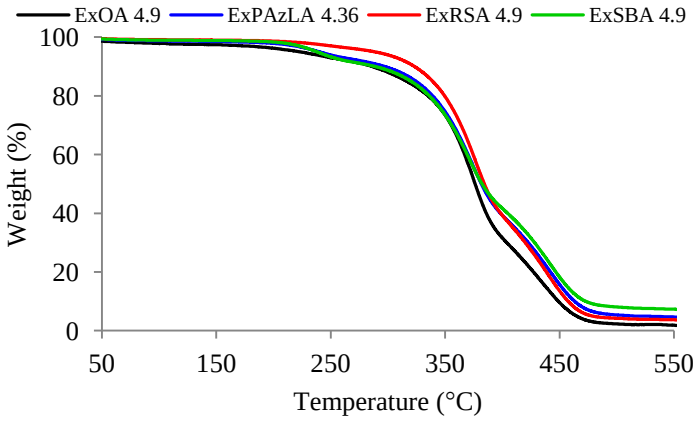
TGA of PEx polymers 4.16.



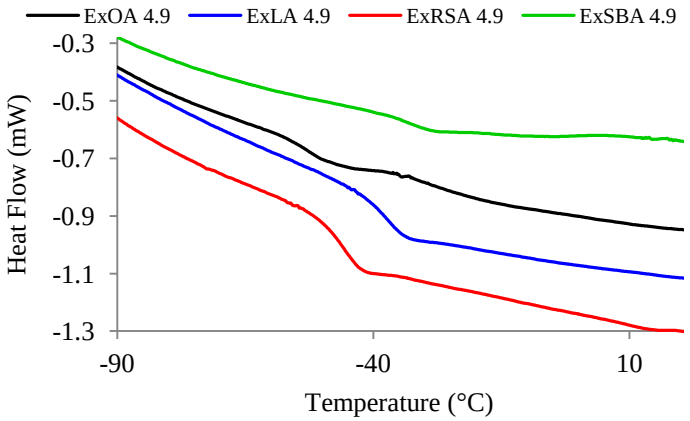
DSC of PEx polymers 4.16 T_g.



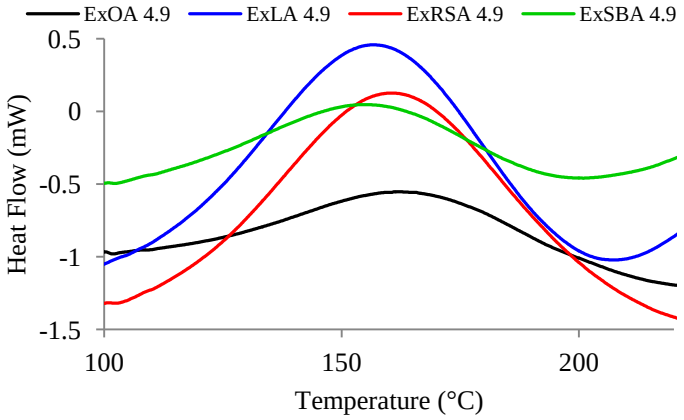
Stress strain curve of PEx polymers



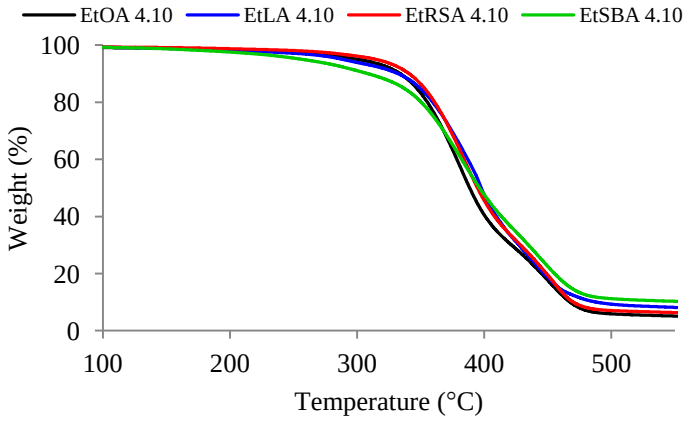
TGA of ExA monomers 4.9



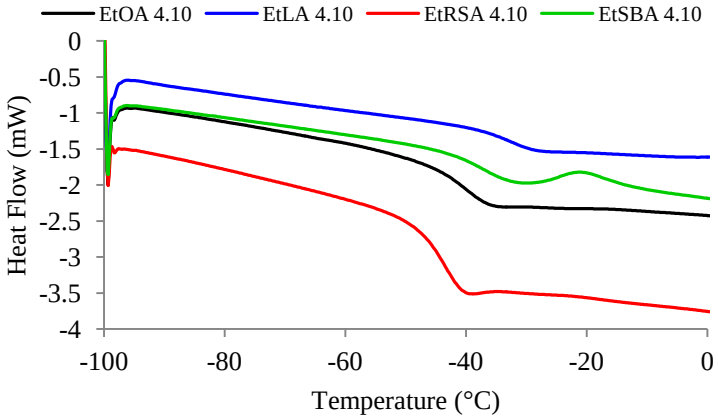
DSC of ExA monomers 4.9 T_g.



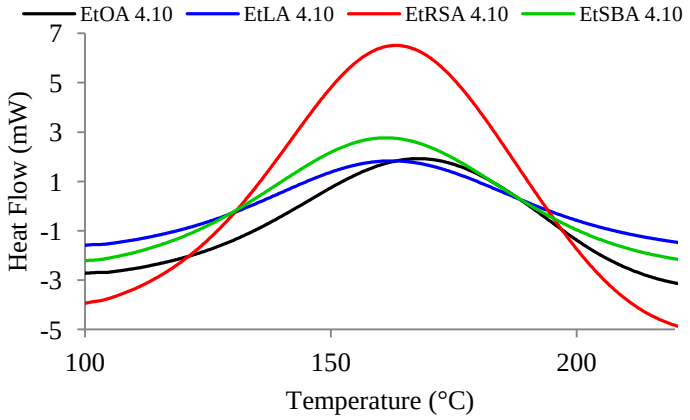
DSC of ExA monomers 4.9 cure point.



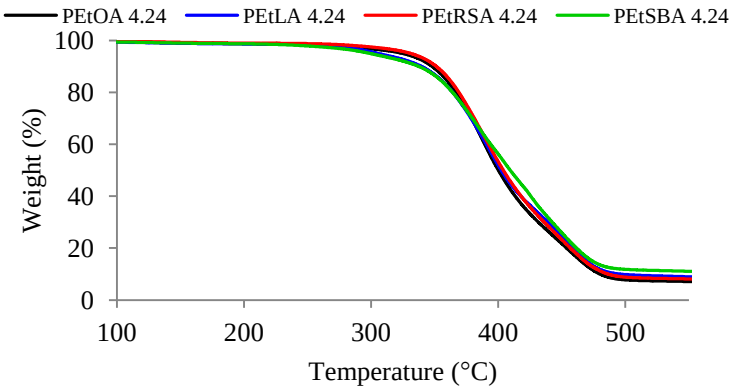
TGA of Et monomers 4.10



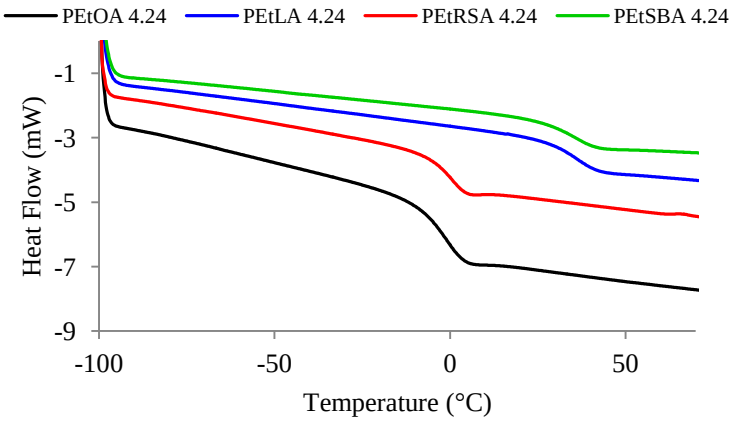
DSC of Et monomers 4.10 Tg.



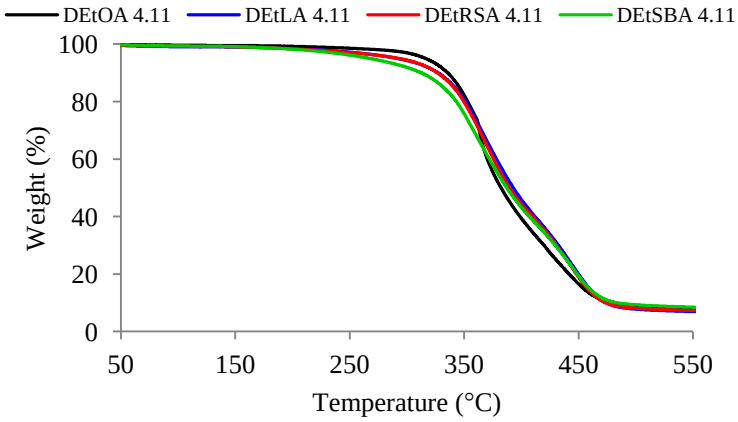
DSC of Et monomers 4.10 cure point.



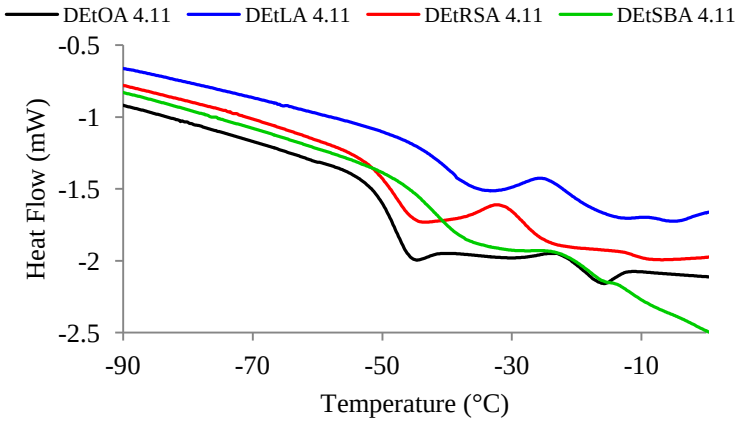
TGA of PEt polymers 4.24



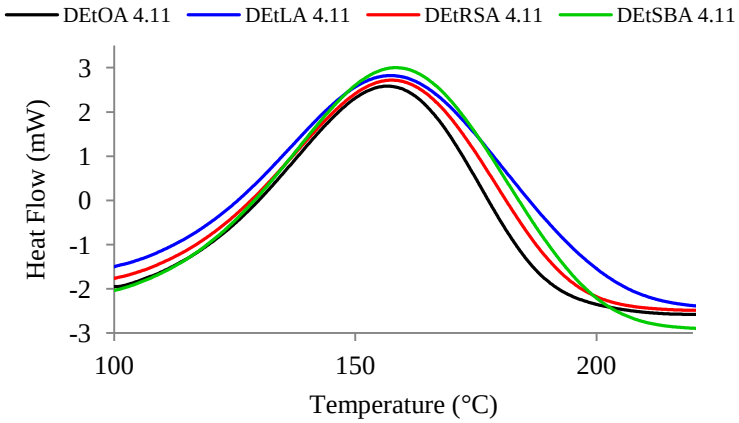
DSC of PEt polymers 4.24



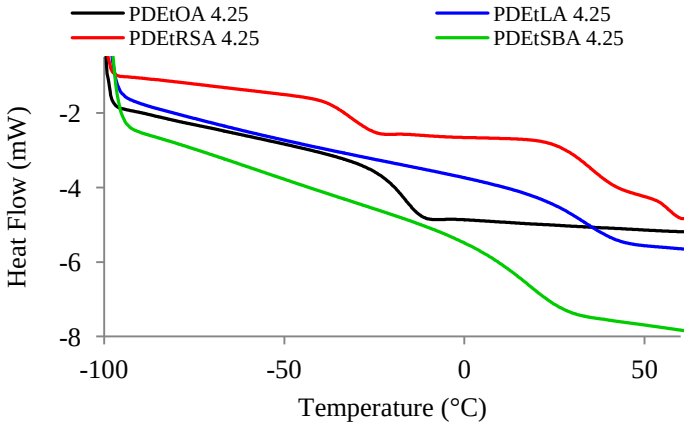
TGA of DEt monomers 4.11



DSC of DEt monomers 4.11 T_g.

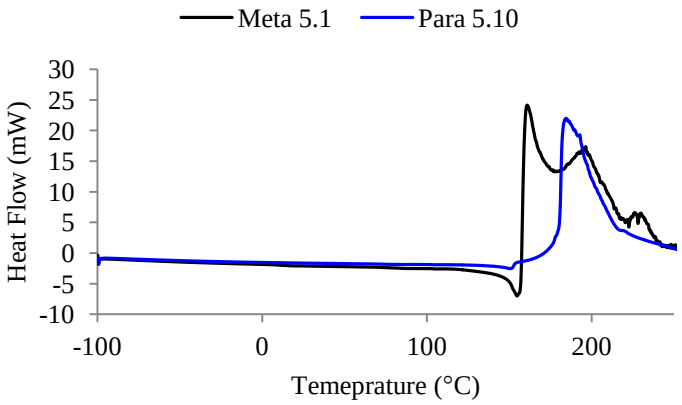


DSC of DEt monomers 4.11 cure point.

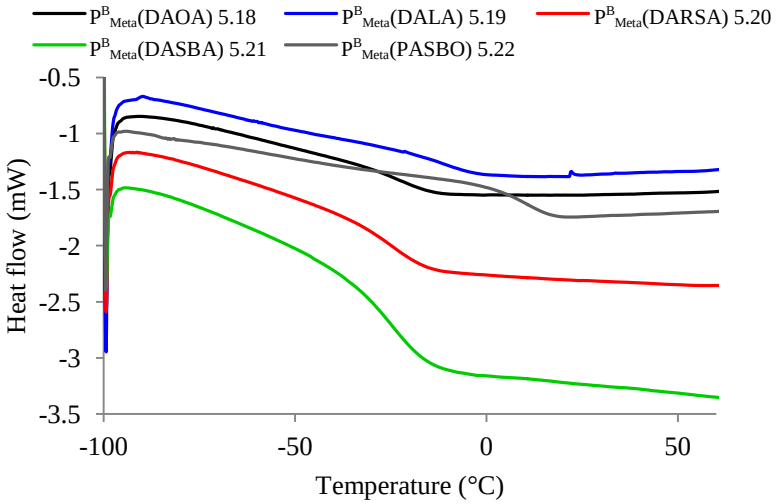


DSC of PDEt polymers 4.25

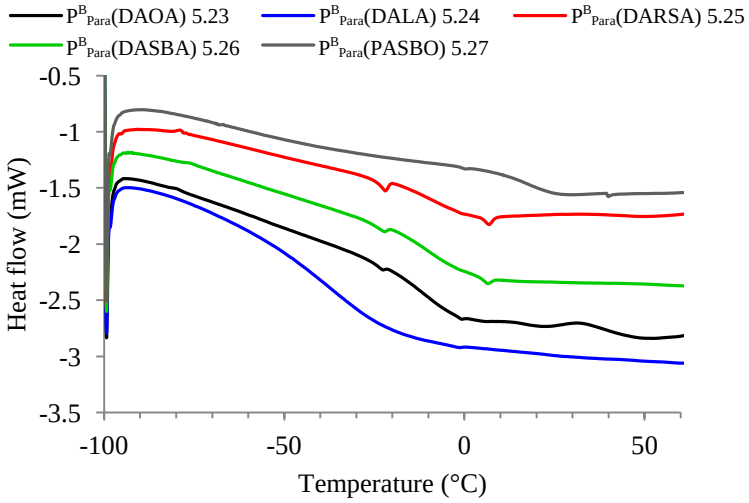
Appendix 4



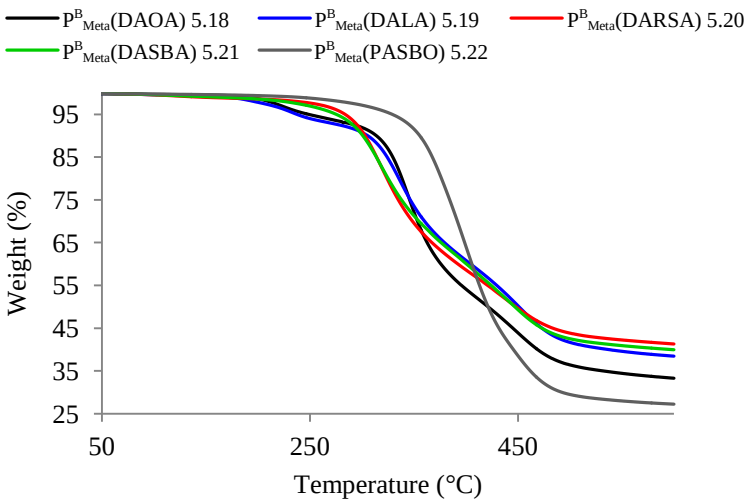
DSC of Nitrile oxide precursors



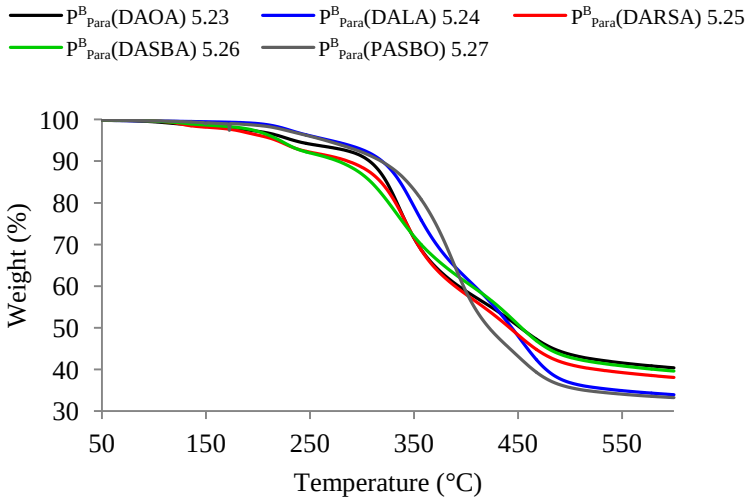
DSC of meta base promoted polymers



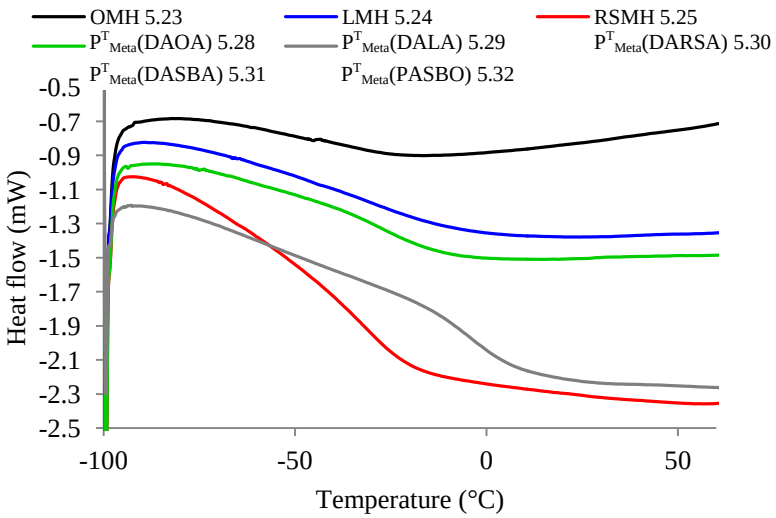
DSC of para base promoted polymers



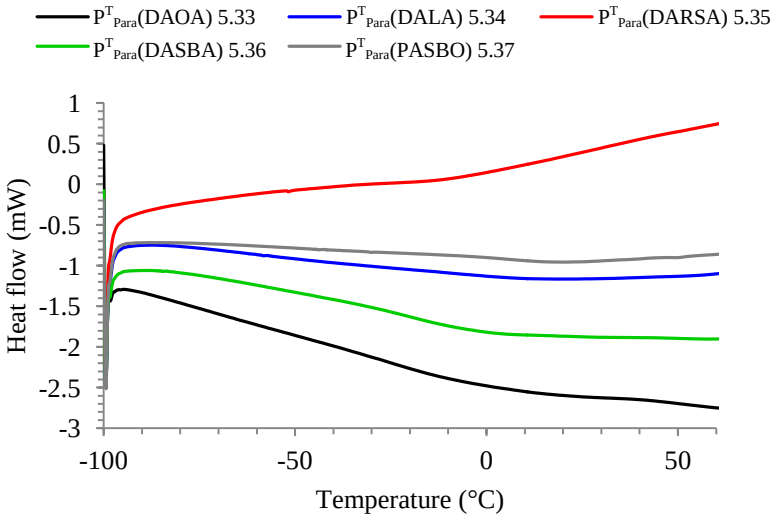
TGA of meta base promoted polymers



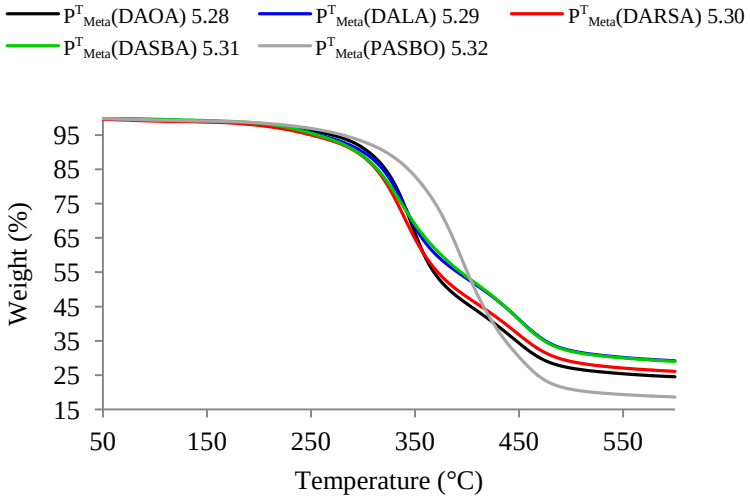
TGA of para base promoted polymers



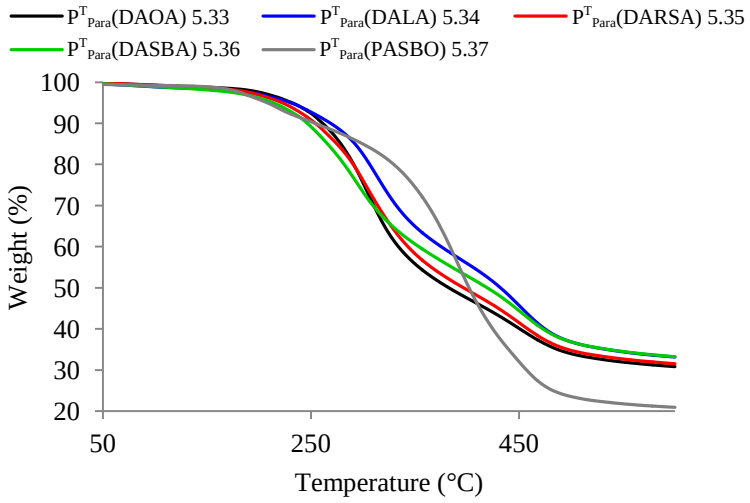
DSC of meta heat polymers



DSC of para heat polymers



TGA of meta heat polymers



TGA of para heat polymers